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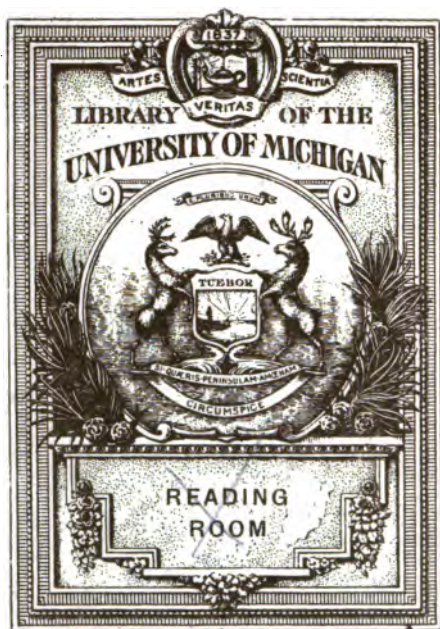
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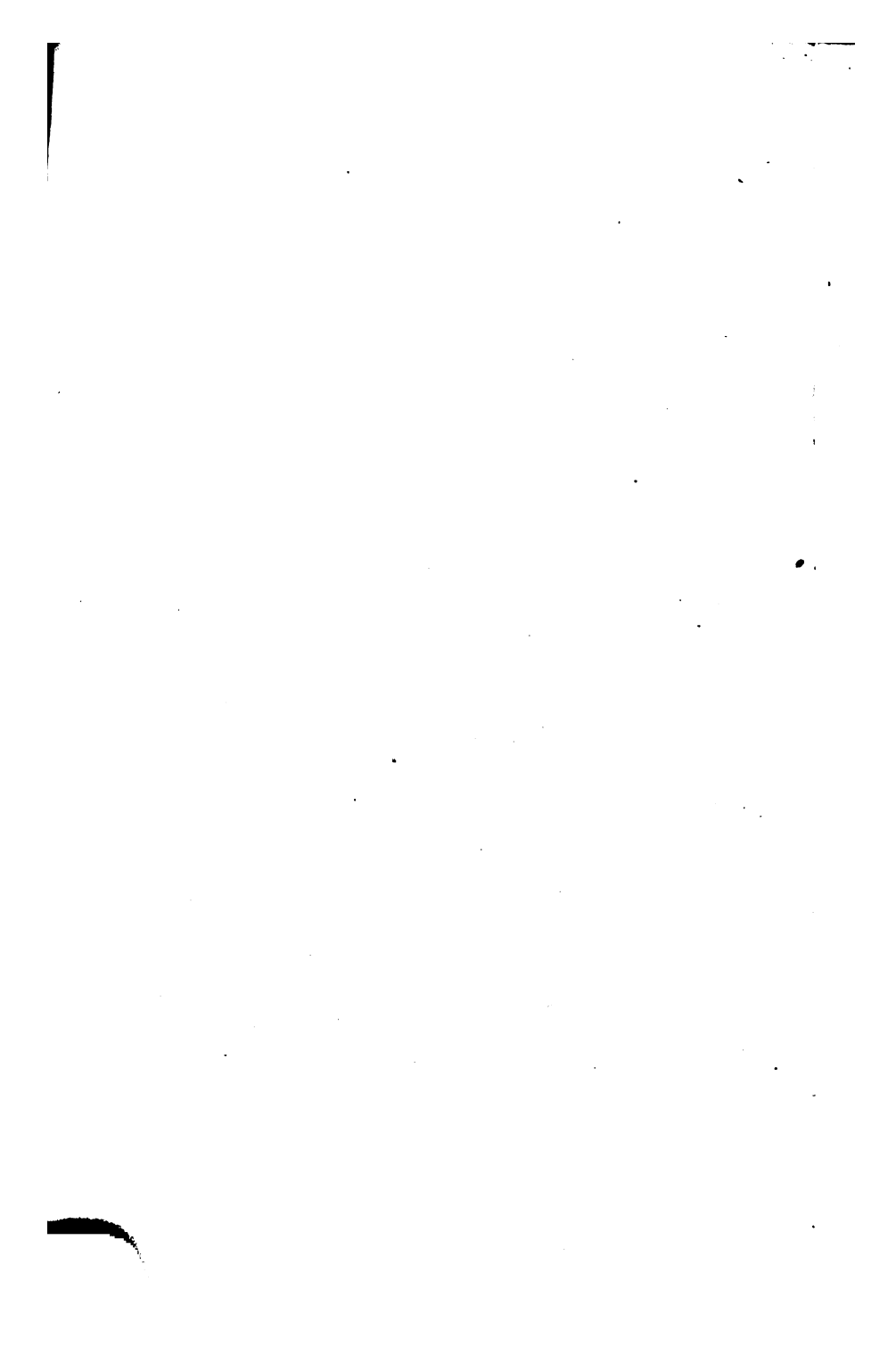
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AN
ELEMENTARY TREATISE
ON
HEAT

BY
BALFOUR STEWART, LL.D., F.R.S.

LATE PROFESSOR OF NATURAL PHILOSOPHY, VICTORIA UNIVERSITY
OWENS COLLEGE, MANCHESTER

Sixth Edition

REVISED WITH ADDITIONS

BY
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STUDENT OF CHRIST CHURCH, OXFORD, AND DR. LEE'S
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its sources, and connexion with other properties of matter. In this part Heat is viewed as a kind of energy, and the leading principles by which Heat becomes related to other forms of energy are discussed.

It may be well to state the basis on which the reasoning of this part has been founded. It has appeared to the Author that the foundation which involves the smallest amount of assumption is that adopted by Professor Sir W. Thomson, namely the denial of the possibility of a perpetual motion of any kind, and it will be shewn in the sequel that the denial of one form of perpetual motion involves the principle of the 'conservation of energy,' while the denial of another form involves the principle of the 'dissipation of energy.'

In our ignorance of the ultimate constitution of matter it would thus appear that both the 'conservation of energy' and the 'degradation or dissipation of energy' should be viewed as principles having very strong claims to recognition, and as increasing these claims every day by the new facts which their employment as instruments of research is constantly bringing to light.

A few words with regard to the mode in which the subject of temperature is viewed. Some eminent philosophers are of opinion that our methods of subdividing a range of temperature are to a great extent arbitrary, so that provided we always adhere to the same method we shall not be led into error.

Be this as it may, there can be no question that some methods of doing this are much more convenient than others; nay, even that one method, that by the air thermometer, enjoys such a pre-eminence of convenience that it may with propriety be termed the proper method of subdividing a range of temperature.

Starting with the assumption that there is a proper method of measuring temperature, it is shewn near the beginning of this work that even if we are ignorant of this proper method there is yet an advantage in employing an air thermometer. This advantage consists in the fact that we may use any permanent gas we choose for our air thermometer, and yet obtain results as nearly as may be identical with one another if all our instruments are read on the same principle ; while, on the other hand, the indications of two thermometers filled with different liquids, and both graduated on the same principle, are not strictly comparable with each other. If we determine to prefer an air thermometer we still have to decide on what principle it ought to be read, and while this principle is indicated at the commencement of the work, the reasons in favour of its adoption are not fully discussed until the end.

The Author cannot omit the opportunity of acknowledging his obligations to several scientific friends for the suggestions and advice they have kindly given him ; more especially is he indebted to the organizing Secretary of this Series of Works at Oxford for much valuable assistance throughout the book.

PREFACE TO THE SECOND EDITION (1871).

IN this edition the Author has noticed those discoveries connected with ' Heat ' which have taken place since his first edition was published. He has also added to the problems at the end of the volume by introducing Sir W. Thomson's applications of the dynamical theory of

'Heat' to the establishment of relations between the physical properties of bodies.

He takes the opportunity of acknowledging his obligations to various scientific friends, and more especially to the Rev. Professor Price of Oxford, for many suggestions while the edition was passing through the Press.

PREFACE TO THE THIRD EDITION (1876).

IN this edition the Author has noticed those discoveries connected with 'Heat' which have taken place since his second edition was published. He has also added to the problems at the end of the volume by introducing, in addition to those already given, articles on 'The Molecular Theory of Gases,' 'The Connexion between the two Elasticities and the two Specific Heats,' 'The Velocity of Sound,' and 'Graphical Representations of Physical Laws.'

PREFACE TO THE FOURTH EDITION (1880).

IN this edition the Author has noticed those discoveries connected with 'Heat,' which have taken place since his third edition was published.

He has also added a discussion regarding spectrum analysis and the likelihood that it may throw light on the ultimate constitution of matter.

PREFATORY NOTE TO THE FIFTH EDITION
(1888).

AT the request of Mrs. Stewart I undertook to read the proofs of this new edition of her late husband's well-known and excellent Treatise.

I found, however, that there was but little to do. Prof. Balfour Stewart had himself given *imprimatur* to all but the last six sheets ; and for these I was furnished with 'copy' (excepting four pages) fully revised and initialed by him.

The book is published, therefore, precisely in the form in which its author intended it to appear.

P. G. TAIT.

PREFACE TO THE SIXTH EDITION (1895).

HAVING been requested by the Delegates of the Press to prepare a new edition of this excellent work, I have revised it throughout. I have especially remodelled the article on critical temperature, and have added articles on the radiomicrometer, bolometer and steam calorimeter, and on the direct determination of the specific heat of gases at constant volume. I have also carefully revised all the calculations.

ROBERT E. BAYNES.



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INTRODUCTION

1. THE word 'Heat' is used in the following treatise to denote that agent which produces a certain well-known sensation when applied to the human body.

2. But this sensation, while so familiar to us that every one must immediately recognize what agent is meant when the term Heat is used, is yet not sufficiently definite or constant to afford us the means of accurately measuring the amount of heat which a body possesses. The same substance may at the same time appear warm to one individual and cold to another; nay, it may even be pronounced warm by one of our hands and cold by the other. Our judgement with regard to the amount of heat possessed by the substance in question is thus found to depend upon the state of our bodies, and, as this changes from time to time, we cannot make use of our sensations as a means of measuring heat.

3. In the study of this subject it is thus of primary importance to become acquainted with some instrument by the aid of which the state of bodies with regard to heat may be accurately determined. The Thermometer fulfils this requirement, and a description of it will therefore form the commencement of this treatise.

4. When the Thermometer has been described, the various effects produced in bodies by the presence of heat may next with advantage be studied. Such effects are change of volume; of condition; of hardness; chemical change; with other effects which will afterwards be mentioned.

5. The laws which regulate the distribution of heat will next be considered, and under this head it will be necessary to recognize two distinct modes of conveyance of this agent from one body to another. Every one is familiar with the fact that the contact of a cold body with a hot one, whether solid, liquid, or gaseous, will cause the latter to part with some of its heat. But this is not the only way by which heat may reach us; for we derive a very considerable amount from the sun, although this luminary is at a great distance from the earth, while the intervening space does not contain that gross form of matter which serves to convey heat by contact.

We are thus taught that a hot body parts with its heat in two ways—

(1) By *contact* with a cold body;

(2) By *radiation* through space.

And we believe, moreover, that radiant heat traverses space with the enormous velocity of 186,000 miles per second.

6. We have thus the means of making a very convenient and easily perceived classification of the modes in which Heat exhibits itself to us.

There is, in the first place, what we may call *absorbed heat*, which resides in a hot body, and often remains in it for a considerable time; and we have, in the next place, *radiant heat*, which is heat in the act of passing through space with a very great velocity.

7. In treating of the laws which regulate the distribution

of heat this distinction may with propriety be observed, and this part of the subject will thus divide itself into two. It will be desirable to consider, in the first place, radiant heat—its nature, and the laws regulating its distribution ; and then to consider the laws regulating the distribution of absorbed heat, while under this last heading the capacity of bodies for heat will be discussed.

8. In treating of radiant heat theoretical views will for the first time be introduced. It is well known that there have been two distinct theories regarding the nature of Heat. In one of these it is viewed as a substance which insinuates itself between the particles of a hot body, while in the other it is regarded as a kind of motion taking place amongst these particles. Such views could not well be introduced at an earlier stage of the work, since the more prominent effects of heat upon bodies form a set of phaenomena that are capable of being explained tolerably well by either hypothesis. They are therefore somewhat unsuitable as tests of a theory, while, on the other hand, they are of extreme importance as facts. But the study of radiant heat enables us to pronounce with a near approach to certainty that this influence is not a substance ejected from a hot body, but a kind of undulatory motion transmitted by means of a medium pervading all space.

9. It would appear to follow, as a corollary from this, that ordinary heat into which radiant heat is transformed when absorbed must also imply a kind of motion, and this view will be abundantly confirmed in the next part of the subject, where the various sources of heat will be treated of, and the nature of this agent as well as its connexion with other properties of matter fully discussed.

10. Lastly, this treatise will contain throughout notices of some of the most important practical applications of the

laws of Heat, and also of certain terrestrial and cosmical adaptations in which these laws play a very important part.

In former Treatises on Heat the term Caloric is frequently used; here it is avoided as much as possible, because it has come to be associated with that theory which regards heat as a substance and not as a kind of energy due to molecular motion.

BOOK I

EFFECTS OF HEAT UPON BODIES



CHAPTER I.

Temperature, and its measurement by Thermometers.

DEFINITION OF TEMPERATURE.

11. THE temperature of a body may be defined to be its state with respect to sensible heat. When the amount of sensible heat in a body increases, its temperature is said to rise; and when this diminishes, its temperature is said to fall. It is expedient to discuss at the outset certain fundamental principles which underlie all measurements of temperature.

12. If there be two substances, as for instance water and mercury, in such a condition that when brought intimately into contact with one another and shaken together neither of them changes its state with respect to heat, then these two bodies may be said to be in a state of equilibrium of temperature with each other. Suppose now that the mercury is in a similar state with respect to a third substance, oil. We have thus the water in equilibrium of temperature with the mercury and the mercury in equilibrium of temperature with the oil. Now we know, as the result of experience, that we shall also have the water in equilibrium of temperature with the oil. In fine, if a series of bodies be in equilibrium of temperature with each other

in any one order they will be so in any other order ; and no matter how they are brought together or mixed up with one another, they will always retain unchanged their state with respect to heat. All such bodies are said to be of the same temperature.

But if when the water and the mercury are brought together the water parts with some of its heat to the mercury, then it is said to be of a higher temperature than the mercury ; and if, on the other hand, the water receives heat from the mercury, then it is said to be of a lower temperature than the mercury.

13. It will be inferred from what we have said that if two bodies of different temperature be intimately associated with one another they will both at length attain one common temperature.

Let us now suppose that we have a large mass of liquid whose temperature we wish to measure by means of a thermometer. Strictly speaking, when the thermometer and the liquid are brought intimately together, an intermediate common temperature will be attained, but if the mass of the liquid be very much greater than that of the thermometer the former will not be appreciably changed in temperature by the immersion in it of the latter, and the result will be that the thermometer will denote with sufficient accuracy the temperature of the liquid—only it is necessary that this instrument be very small. But if the temperature of the liquid be kept constantly recruited by some natural process, as for instance that of boiling, the thermometer will in such a case, whatever be its size, at length attain the temperature of the boiling liquid in which it is immersed ; but a small thermometer will attain this temperature sooner than a large one.

14. **Requirements to be fulfilled by a good Thermometer.** Having stated these facts, let us now point out the

requirements which an instrument for measuring temperature may be expected to fulfil. 1st, it ought to be of small size and easily portable. 2nd, it ought always to give the same indication for the same temperature, or be capable of doing so by a simple correction. 3rd, it ought to do something more than merely denote that one body is hotter or colder than another, it ought to *measure* the difference of temperature. For the difference between two temperatures, such as the freezing and the boiling points of water, is one which we conceive to be capable of accurate subdivision into any number of equal parts, which form as it were successive equal steps by which we may mount, from the lower to the higher temperature. This last requirement is the most difficult one, for it implies not only a knowledge of the agent Heat, but also of the changes which it produces upon bodies, since we must evidently make use of some one of these changes in the construction of our instrument for measuring temperature.

While a mercurial thermometer may probably be so made as to fulfil the first and second of these requirements, it is an air thermometer which will best satisfy the third; but the reasons which lead us to suppose that this instrument gives us the means of measuring temperature with great accuracy cannot well be discussed at the outset of this work. These will be given hereafter: in the meantime, let us take it for granted that an air thermometer does really fulfil this requirement, and refer our readers for a description of this instrument to our chapter on the dilatation of gases (see Art. 67).

15. But while an air thermometer gives a very correct indication of temperature, it is nevertheless an instrument difficult of construction and awkward in use: it ought therefore to be employed rather as a standard of reference, by means of which the errors peculiar to some other

instrument of easy construction and simple form may be determined.

MERCURIAL THERMOMETER.

16. An instrument of this kind is found in the mercurial thermometer, which is constructed upon the principle that mercury when heated expands very much more than glass.

In making a mercurial thermometer a tube of glass is selected which has a capillary bore, and a bulb is blown at one extremity of it, the other end of the tube being left open to the atmosphere. The bulb is then heated so as to drive out some of the air which it contains, and the open end of the tube is inserted into a basin of pure mercury. As the bulb begins to cool and the pressure of the air within it diminishes, part of this mercury will be driven up the bore into the bulb. The mercury thus driven into the bulb is then boiled, and the mercurial vapour drives away any air or moisture that may have adhered to the tube. While the instrument is hot and full of the vapour of mercury its extremity is once more plunged into the basin of mercury, by which means, on condensation of the vapour, the bulb and tube will be filled with mercury. When the tube is still hot and full of mercury it is hermetically sealed, and when the instrument has cooled the mercury will be found to fill the bulb and part of the stem, the other part being empty. If now the bulb of this instrument be heated the glass envelope will expand, and also the mercury with which it is filled; but the mercury will expand much more than the glass envelope, and in consequence the mercurial column will rise in the capillary tube. If the bore be fine enough, a considerable rise may thus be produced even when there is only a small expansion

of the mercury, and by this means a very great amount of delicacy may be given to the instrument.

17. Calibration of the tube. If the instrument is to be as accurate as possible, it is necessary to know the relative diameter of the bore at different parts of its length, since this is always variable even in the best tubes.

To accomplish this the tube is made by the glass-blower in such a way that by a simple mechanical contrivance a small column of mercury, occupying the length of about one-third of an inch in the bore, may be detached from the main body of the fluid. This column is then made to travel from the one extremity of the tube to the other, and its length is measured by a microscope at each short stage of its progress. It is obvious that this column will be long where the bore is narrow, and short where it is wide, and that by this means we may obtain the relative diameter of the bore in different parts of the tube. The detached column having served its purpose is now reunited to the main body of the mercury. It will be afterwards seen (Art. 20) in what manner the information thus obtained is made use of.

18. Determination of the fixed points. The freezing-point. Our object in constructing a thermometer presupposes the existence of at least two fixed points of temperature. The two universally adopted are the freezing and the boiling points of water. Suppose that a substance ascends from the lower to the upper of these temperatures through a certain number of equal stages or degrees, it is the office of the ther-

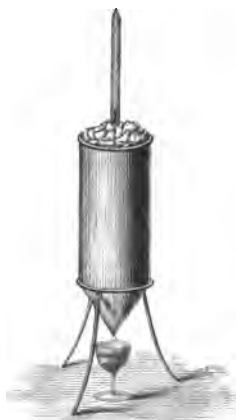


Fig. 1.

mometer to indicate these. In order to determine the lower fixed point, a box or vase (Fig. 1) is perforated in the bottom with a few holes to permit drainage, and placed in a room whose temperature is above the freezing-point of water. It is then filled with snow or pounded ice in a melting state, and it has been ascertained that the temperature of this melting ice is under ordinary circumstances virtually constant. The thermometer is now placed vertically in this mixture, the ice being heaped about the stem, and is so left for a quarter of an hour, or until the mercury has become stationary. The tube is then marked with a scratch at the termination of the mercurial column, and the lower of the two points is thus determined. Presuming that Fahrenheit's scale is to be employed, this point will denote 32° .

19. The boiling-point. The next process consists in determining the boiling-point of water. This, unlike the freezing-point, is not virtually constant, for the temperature of steam in contact with water depends upon, and alters considerably with, the pressure under which it exists.

It had been observed by Gay-Lussac that water boils under the same pressure at slightly different temperatures in different vessels; but Rudberg afterwards found that the nature of the containing vessel altered only the temperature of the water and not that of the steam. It is therefore in steam, not water, that a thermometer ought to be plunged in order to have its upper point determined. Hence also if steam escape from an open vessel containing water into the air, the temperature of the steam, which depends upon the pressure under which the steam exists, will therefore depend upon the atmospheric pressure, since this must be the same as that of the steam. The temperature of the steam of water boiling in an open vessel will therefore vary with the barometer; but if we know the law of this

variation we can make allowance for it in graduating our thermometer.

The Commissioners appointed by the British Government to construct standard weights and measures, and the Kew Committee of the British Association, have both agreed that the upper point of a thermometer graduated according to Fahrenheit's scale, or that hitherto adopted in this country, shall be taken to represent at London the temperature of steam, at the pressure of 29.905 inches of mercury reduced to the freezing-point¹. This is therefore the true meaning of 212° Fahrenheit, and the temperature of steam at other pressures may be found from the following table.

Temperature in Fahrenheit degrees of steam at different pressures (at London).

Temperature.	Pressure in inches of mercury at 32° Fahr.	Temperature.	Pressure in inches of mercury at 32° Fahr.	Temperature.	Pressure in inches of mercury at 32° Fahr.
211.0	29.315	211.7	29.727	212.4	30.143
211.1	29.374	211.8	29.786	212.5	30.203
211.2	29.432	211.9	29.845	212.6	30.263
211.3	29.491	212.0	29.905	212.7	30.323
211.4	29.550	212.1	29.964	212.8	30.384
211.5	29.609	212.2	30.024	212.9	30.444
211.6	29.668	212.3	30.083	213.0	30.504

We are thus furnished with the means of determining the higher point. Let the instrument be immersed in steam arising from boiling water, mark off as before the termination of the mercurial column, reading the barometer at the same moment. If the pressure of the atmosphere be 29.905 inches, this point will denote 212°; and for any other pressure the true value of the mark may be found from the above table.

¹ That is to say, the density of the mercury being that which it has at 32° Fahr.

In performing this operation it will be found most convenient to employ Regnault's apparatus (see Fig. 2). The arrangement will best be perceived from Fig. 3, which represents the interior of the instrument.

A is a thermometer having its bulb a little above *E*, the level of the boiling water. The course which the steam is forced to take is denoted by the arrow-heads. It is thus seen that the steam must pass up along the thermometer tube and down again, until finally it leaves the apparatus



Fig. 2.

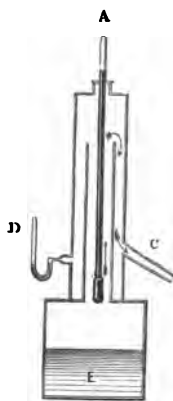


Fig. 3.

by the orifice *C*. The whole of the tube of the instrument is thus thoroughly surrounded by steam, and by a cylinder

having the temperature of the steam. *D* is a bent glass tube, open to the atmosphere, and containing a little water, which shows by a difference of level in the two limbs if the pressure of the steam in the interior is greater than that of the atmosphere without. It has been ascertained that, if the orifice is sufficiently wide, this difference is too small to affect the temperature of the thermometer, and thus the gauge *D* may be dispensed with.

The thermometer is inserted through a closely fitting slit in a thick piece of india-rubber which rests upon the top of the apparatus, and the stem is lowered until the column of mercury just appears above the india-rubber; and thus nearly all the column as well as the bulb is exposed to the vapour of boiling water. This apparatus is generally formed of copper, and distilled water should if possible be used.

20. Graduation. Fahrenheit's scale. The relative diameter of the bore at different parts of the tube having now been determined by calibration (Art. 17), and the two fixed points marked, it is easy to graduate the instrument. If the scale is to be that of Fahrenheit, the lower point is called 32° and the upper point (provided the atmospheric pressure be 29.905 inches) 212° . There are thus 180 divisions between the two points, and these are marked upon the tube in the following manner. The whole instrument is covered over with wax sufficiently thin to allow the two marks (previously blackened) to be visible, and a needle attached to a dividing engine scratches the graduations in the wax. The thermometer is then exposed to hydrofluoric acid or its vapour, which attacks the glass where the wax has been scratched off. The length of each degree is regulated by the previously determined diameter of the bore, in such a manner that the internal capacity of the tube between the two marks is divided into 180 equal parts. The graduation is generally extended below the

freezing-point, and sometimes above the boiling-point. In this thermometer a temperature 32° below the freezing-point is termed *zero*, while one ten degrees lower is called *minus* 10° , or 10° below *zero*, and so on.

21. Other scales. Besides Fahrenheit's scale there are two others, those of Celsius and Réaumur. The former of these is also called Centigrade, and is used throughout France; the latter is in very general use in Germany.

In the Centigrade thermometer the freezing-point of water is termed 0° , or *zero*, while the boiling-point is reckoned equal to 100° . A degree Centigrade is therefore greater than a degree Fahrenheit in the proportion of nine to five. The boiling-point in this thermometer, or 100° , is defined by Regnault to be the temperature of steam under the barometric pressure of 760 millimètres, or 29.922 inches, of mercury reduced to the freezing-point of water at the latitude of Paris. This is slightly different from the corresponding point, or 212° , in Fahrenheit's scale, which, as we have seen, denotes the temperature of steam under the pressure of 29.905 inches of mercury reduced to 32° at the latitude of London. It must, however, be borne in mind that the intensity of gravity, and therefore the absolute attraction towards the earth of the same mass of matter, is somewhat greater in London than in Paris, so that 29.922 inches of mercury in Paris are equal in absolute pressure to 29.913 inches at London (see Art. 143). This still leaves a slight difference between the absolute pressure of the steam in the two cases, and hence the upper points of these two instruments will not quite correspond in temperature; but this difference is so very small that for ordinary purposes it may be neglected.

Inasmuch as Centigrade thermometers are those most frequently made and used by scientific men, it will be desirable to give the temperature of steam in Centigrade

degrees corresponding to various atmospheric pressures, these pressures being recorded either in millimètres or inches of mercury reduced to the freezing-point. This is done in the following table:—

Temperature in Centigrade degrees of steam at different pressures (at Paris).

Tempera- ture.	Pressure		Tempera- ture.	Pressure	
	in inches of mercury.	in milli- mètres of mercury.		in inches of mercury.	in milli- mètres of mercury.
99.0	28.867	733.19	100.0	29.922	760.00
99.1	28.971	735.84	100.1	30.029	762.73
99.2	29.075	738.49	100.2	30.137	765.46
99.3	29.180	741.15	100.3	30.245	768.20
99.4	29.285	743.82	100.4	30.353	770.95
99.5	29.390	746.50	100.5	30.461	773.71
99.6	29.496	749.18	100.6	30.570	776.47
99.7	29.602	751.87	100.7	30.680	779.25
99.8	29.708	754.57	100.8	30.789	782.03
99.9	29.815	757.28	100.9	30.899	784.82

To reduce Fahrenheit to Centigrade the following formula is made use of, $C = (F - 32) \frac{5}{9}$; while to reduce Centigrade to Fahrenheit we have $F = \frac{9C}{5} + 32$.

Thus, were it required to find what degree Centigrade corresponds to 77° Fahr., we should proceed in the following manner. Subtracting 32° from 77° we find that this temperature is 45° above the freezing-point, or Centigrade zero, and taking $\frac{5}{9}$ of 45°, since Centigrade degrees are greater than those of Fahrenheit in the proportion of 9 to 5, we find that 25° Cent. corresponds to 77° Fahr.

Again, were it required to find what degree Centigrade corresponds to -38.2 Fahrenheit, we should have, as above—

$$C = (-38.2 - 32) \frac{5}{9} \quad \text{or} \quad C = -70.2 \times \frac{5}{9} = -39^\circ.$$

In the scale of Réaumur the distance between the freezing- and boiling-point is divided into 80 parts, and the boiling-point is defined to be the temperature of steam under the pressure of 760 millimètres of mercury, the intensity of gravity being that which corresponds to latitude 45° .

This pressure corresponds as nearly as possible to that of 29.905 inches of mercury reduced to the freezing-point at the latitude of London, and hence the boiling-points of Fahrenheit and Réaumur represent the same temperature.

To reduce Fahrenheit to Réaumur we have therefore the following expression, $R = (F - 32) \frac{4}{9}$; while to reduce

Réaumur to Fahrenheit we have $F = \frac{9}{4} R + 32$. It will readily appear that the Centigrade scale is much more convenient than either of the other two: we shall therefore employ it in the various calculations of this treatise.

22. Correction for change of zero. It is found that thermometers are liable to an alteration of their zero points, especially when the bulb has been filled not long before graduation. This displacement is of the following nature. Immediately after graduation 0°C will of course denote the temperature of melting ice; but when some time has elapsed a thermometer placed in melting ice will no longer give this reading, but one somewhat higher, perhaps 0.2 or 0.3.

When an instrument has been graduated shortly after the filling of the bulb, this displacement may in the course of years amount to about 1°C , but it is believed that this is the extreme limit of the change. But if the bulb has been kept for some time before graduation, and has also been well annealed, the change is much less: nevertheless it may possibly amount in the course of years to three or four tenths of a degree Centigrade. Besides this progressive and permanent change there is also a temporary

one, produced by heating and suddenly cooling the instrument. For instance, if a thermometer have first of all its freezing-point determined by melting ice, if it then be plunged into boiling water, then suddenly withdrawn, and finally plunged again into ice, the freezing-point will be found to have changed—the instrument may now read -0.1 , and it will not recover its true reading until several weeks or months have elapsed. On this account it used to be the invariable custom to mark off first the freezing-point and then the boiling-point in constructing a standard thermometer. An opinion has subsequently, however, arisen amongst meteorologists that the position of the freezing-point of an instrument that has recently been plunged into boiling water is the most constant thing of the kind that can be procured. This maximum depressed freezing-point has in consequence been provisionally recommended by the Congress which met in Rome in 1879.

In February 1883 the Kew Committee proposed, in the case of high-range chemical thermometers, to adopt this maximum depressed freezing-point as the zero of their centigrade scales, but this body have not adopted the new system for ordinary thermometers. The opinion of the writer of this volume is in favour both of the action of the Kew Committee and of its limitation.

To correct for change of zero the thermometer ought to be plunged from time to time into melting ice, and its reading noted. The amount of alteration thus becomes known, and the requisite correction may be applied, which is of course constant throughout the scale.

23. Other sources of error. If a thermometer have its fixed points determined in a vertical position it must always be used in this position; in like manner, if these points are determined in a horizontal position of the instrument, then it must always be used horizontally.

The reason of this is, that for the same temperature the same instrument will give a higher reading in a horizontal than in a vertical position, since in the latter the hydrostatic pressure of the column of mercury will tend not only to compress the particles of mercury into less volume, but also to enlarge the capacity of the bulb.

For a similar reason the reading of an unprotected thermometer in vacuo will be different from its reading in air.

24. Again, when the volume of mercury in the stem of a thermometer is exposed to a temperature different from that of the bulb, a correction must likewise be made on this account.

For instance, if the bulb and the column of mercury up to freezing-point mark have the temperature of boiling water, while the remainder of the column is exposed to the atmosphere, which we may imagine to be at 0°C , then the instrument will not indicate 100°C . It would have done so had the whole of the mercury been heated up to the boiling-point, but this is not the case, for nearly 100 degrees, or the distance between the freezing-point mark and the extremity of the column, is exposed to the atmosphere, and may be taken to have the same temperature as it has.

In order to find the correction which we ought to apply, let us denote by unity the whole volume of the mercury when it is all at the temperature 0° : unity will therefore also denote the internal capacity at this temperature of the glass envelope up to freezing-point mark. Now it will be afterwards shown (Art. 52) that this mercury when raised to 100° will have the volume 1.01815 nearly, and also (Art. 40) we may perhaps suppose that the internal capacity of the glass up to freezing-point mark will have, when raised to 100° , the volume 1.00258: this however depends upon the nature of the glass. Hence a volume of mercury equal to

1.01815—1.00258, or .01557, will exist in the tube above the freezing-point mark provided that the *whole column* of mercury be heated up to 100°; and it will under these circumstances occupy 100 degrees of the bore. The question to be answered is, how many degrees of the bore will this portion of mercury occupy when both it and the tube containing it are at 0°? Evidently the absolute volume of this portion of mercury at 0° will be $.01557 \times \frac{1}{1.01815} = .01529$.

Hence if we imagine the bore of the tube to preserve a constant volume for all temperatures, the rise may easily be found. For if the volume .01557 occupy 100 divisions, the volume .01529 will occupy $100 \times \frac{.01529}{.01557}$ or 98.22 divisions.

But the bore of the tube in which this rise takes place does not preserve a constant volume throughout, but, being only at 0°, is really of smaller capacity than it was at 100°, in the ratio of 1 to 1.00258: the rise of 98.22 will therefore have to be increased in this proportion, and will become 98.47, or the mercury will indicate this as the boiling-point of water; a correction of +1°.53 must therefore be applied. If the thermometer be a Fahrenheit one the correction will be $+1°.53 \times \frac{9}{5} = +2°.75$.

This example will convey to the reader sufficiently well the method to be employed in finding this correction, but it ought to be borne in mind that it is much better when practicable to avoid the necessity for it, by exposing the whole column of mercury as well as the bulb to the influence of the temperature which we wish to estimate.

25. Lastly, even when a mercurial thermometer has been constructed with the greatest accuracy after the method indicated in the preceding articles, so that the freezing-point is denoted by 0° and the boiling-point by 100°, while each

degree denotes precisely the 100th part of the capacity of the bore between these two points, it does not follow that the instrument will give an intermediate temperature with absolute exactness.

For, in the first place, it does not follow that the expansion in volume of the mercury above that of the glass envelope up to freezing-point mark for a true rise of 50° must be precisely half of its expansion for a true rise of 100° .

In the next place, it ought to be borne in mind that the rise of 50° takes place in a bore of which the temperature is only 50° , and of which therefore the capacity is smaller than when the temperature is 100° , in the proportion of 1.00129 to 1.00258.

Both of these circumstances will introduce errors, and Regnault has found that when the graduation is extended much above 100° , the difference between the mercurial and the standard air thermometer becomes very considerable at high temperatures, and also varies with the nature of the glass. But between 0° and 100° , and for a range extending not too far beyond these points, a mercurial thermometer well graduated may be considered to be a tolerably good though not a strictly accurate instrument. Since the best thermometers are now all formed of the same kind of glass, a comparison of the readings of such thermometers with those of an air thermometer, in which hydrogen has been substituted for air, has been made by M. Chappuis for the International Office of Weights and Measures (see Art. 67).

OTHER THERMOMETERS.

26. Alcohol Thermometer. It is well known that mercury freezes at about -39°C , while it boils at about 349°C . A mercurial thermometer cannot therefore be used below the former point or above the latter. But

while the superior limit of its accurate employment is considerably below the higher temperature, its indications may probably be relied upon very nearly to the point at which the mercury freezes. It is, however, often desirable to register still lower temperatures, and in order to do so a thermometer filled with absolute alcohol is employed. Such an instrument is not capable of being constructed with the same amount of exactness as a mercurial thermometer; but yet if it be carefully made, and used with caution, very good results may be obtained. An alcohol thermometer ought before graduation to be marked off at 0°C , and at some higher temperature by comparison with a mercurial standard thermometer. The freezing-point of mercury ought also, if possible, to be made use of as a fixed point; and it has been ascertained that this, like the freezing-point of water, is of constant temperature, its true value, on the Centigrade scale, being $-38^{\circ}.8$. An alcohol thermometer may be used for very low temperatures, since this fluid has not yet been frozen.

When a very accurate determination is desired, this thermometer should be kept in a vertical position, bulb downwards, for some time before it is read.

The reason of this is that alcohol, unlike mercury, wets the capillary glass tube which contains it, and is also very volatile; great care ought therefore to be taken that there is no liquid above the main column, whether condensed or adhering to the sides of the tube.

27. Maximum and Minimum Thermometers. Maximum. It is often of importance to know not merely the present temperature, but likewise the highest or lowest point to which an instrument has been exposed. Meteorologists, for instance, should be able to register every evening and morning the highest and lowest temperatures of the atmosphere. This when not accomplished by

a continuous photographic registration of temperature, is done by maximum and minimum thermometers.



Fig. 4.

In Rutherford's maximum thermometer the stem is placed in a horizontal position, and the bore contains a small index made of iron or graphite, which the mercury pushes before it when it expands through increase of temperature; but when it retreats this index is left behind, since there is no cohesion between it and the mercury. In Professor Phillips' maximum thermometer this index is part of the mercurial column itself, which, as in Fig. 4, is separated from the main body of the fluid by a little air. When the mercury expands, the elastic force of the air pushes the index on before it; but this is kept in its position when the mercury again contracts. By this arrangement there is no risk of the index soiling the mercury or becoming entangled with it. It has also been found that when the bore is sufficiently narrow the instru-

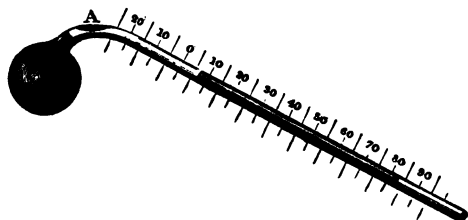


Fig. 5.

ment may be used in a vertical position, bulb downwards, and it is thus of service in chemical operations. Both of these maximum thermometers when read must be reset by

shaking the index down towards the mercurial column as far as it will go.

Negretti and Zambra's maximum thermometer is exhibited in Fig. 5. When used the stem of this instrument ought to be inclined downwards. The bore is nearly choked at *A* by means of a bit of enamel or glass. When the mercury expands, it does so with sufficient force to push its way past this obstruction; but when it contracts, that part of the column past the obstruction is kept there, and the contraction takes place by the mercury to the left of *A* withdrawing into the bulb. It does not matter if the column past the obstruction go down to the bottom of the tube, for when the instrument is read it is gently tilted up until this detached column flows back to the obstruction, where it is arrested, and the end of the column will then denote the maximum temperature. In resetting the instrument it is necessary to shake the detached column past the obstruction, in order to fill up the vacancy left by the contraction of the fluid after the maximum had been reached.

Of late years the principle of this maximum thermometer has been extensively employed in the production of clinical thermometers used chiefly for determining the temperature of the blood.

The following diagram will show the form and size of these little instruments, which have a very open scale between 95° and 113° Fahr., no greater range of temperature being necessary.

28. Lens-front Thermometers¹. The object of these



Fig. 6.

¹ For descriptions of the lens-front and of the avitreous thermometers, I am indebted to G. M. Whipple, Esq., late director of the Kew Observatory.

instruments is to facilitate the readings of such ordinary mercurial thermometers as have extremely fine bores, with the view of providing them with open scales.

Instead of the usual cylindrical stem with the bore in the centre the stem of a lens-front thermometer is approximately prismatic, being an equilateral triangle in section, with the bore very close to the base of the triangle. The apex being rounded off becomes with the sides a lenticular surface of short curvature and correspondingly short focal length, and the bore being situated close to the focus the arrangement resembles a Coddington or Stanhope lens, magnifying the mercurial column in the bore about fifteen diameters.

It is thus rendered clearly visible to the unassisted eyesight, dispensing with the employment of a pocket lens, which cannot be used without difficulty in ordinary instruments on account of difference of focal distance of column and scale.

This form is largely employed for clinical and solar radiation thermometers, in both of which a small bulb is a matter of importance.

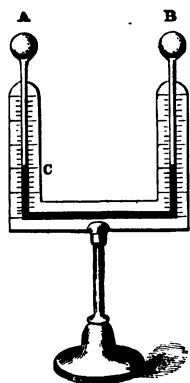


Fig. 7.

20. Leslie's differential Thermometer. Sir John Leslie has constructed an instrument for showing the difference in temperature between two neighbouring substances or places, which is hence called the differential thermometer. In this instrument two bulbs, *A* and *B*, filled with air, are

connected together by means of a bent tube, as in Fig. 7 : a little coloured liquid fills the lower part of this tube; and rises to the levels *C* and *D* when both bulbs are of the same temperature. But should *A* become warmer than

B, since air expands very much for an increase of temperature, the column of liquid will be pushed down at *C* and made to rise at *D*; and this motion will be reversed when *B* becomes warmer than *A*. Such an instrument will therefore indicate any difference of temperature with great delicacy. The fluid in the tube ought to be one which is not volatile—sulphuric acid is frequently used. We shall find afterwards (Art. 165) that the thermo-pile registers any difference of temperature with still greater delicacy than this instrument.

30. Fluctuation Thermometer. The author of this work has proposed an instrument for summing up fluctuations of temperature. If a bulb be blown connecting together two horizontal glass tubes of different bores, and if this instrument be nearly filled with mercury, it will be found that this fluid will expand in the tube of wide bore when the temperature rises, and contract in the other when it falls. Thus the mercury will gradually travel toward the extremity of the tube of wide bore, and its position from time to time will indicate the amount of fluctuation which the temperature undergoes. This instrument is however difficult of construction.

31. Avitreous Thermometers. These instruments, of comparatively recent introduction into science, have been found of great service for measuring temperatures not extending over a very wide range, such as we have in meteorological and clinical observations.

As the name indicates, glass is not employed in their construction, and therefore they can stand rough usage without being broken.

The principle upon which they act is as follows: a thin flexible metal tube is taken and filled with a highly dilat-able fluid, usually a mixture of alcohol and chloroform.

It is then hermetically sealed at both ends and either

twisted, or bent into an arc of a circle, at a low temperature, after which any increase of volume of the liquid will cause the tube to uncoil or untwist so as to increase its internal capacity. One end being rigidly fixed, the motion of the other is rendered visible by an index caused to move over a scale or by a stylus traversing a sheet of paper. The invention was originally due to Bourdon, but its adaptation to a meteorological recording instrument has been brought about by the brothers Richard of Paris, and its introduction to give us a convenient pocket thermometer by Immisch of London, who by the attachment of a maximum index has fitted his instrument for use as a clinical thermometer. Numerous tests of these instruments have been made in various verification offices with excellent results.

31 a. Other instruments for measuring temperature. Wedgwood's pyrometer is an instrument for measuring high temperatures, and its action depends on the contraction which takes place in baked clay when heated.

Dr. C. W. Siemens in 1871 proposed a serviceable pyrometer consisting of a coil of fine platinum wire contained in a cylindrical case. This fine wire forms part of an electric circuit, the intensity of the current thereof being measured by a galvanometer or other appropriate instrument. If this pyrometer be thrust into a furnace the heated coil will increase in electrical resistance, and hence the intensity of the current will be diminished. The indications of the galvanometer or other instrument which measures the intensity of the current will thus afford a measure of the increase of resistance of the coil, and therefore of the temperature of the furnace. By the use of pure platinum and of mica as the insulator, Mr. Callendar has rendered this pyrometer an exceedingly sensitive and trustworthy thermometer through a very wide range of temperature.

The application of Siemens' principle to the construction of the bolometer—an exceedingly delicate instrument for measuring radiant heat devised in 1881 by Prof. Langley—will be described in a future part of this work (Art. 168 a).

Again, in measuring the temperatures of oceanic depths where the pressure is very great an ordinary thermometer would be rendered useless or perhaps broken. In this case the following plan has been adopted. The bulb of the thermometer is enclosed in another stout glass bulb, the space between them being nearly but not quite filled with mercury. It will be apparent that the pressure of the water will in this case only affect the outer bulb, and if this be sufficiently strong to remain whole no pressure will be communicated to the inner bulb which is the true bulb of the thermometer. It will therefore give a correct indication provided the instrument be left long enough in its position to enable the inner bulb to attain the temperature of the surrounding water.

Bréguet's metallic thermometer is another instrument which may be used in measuring temperature, but a description of it must be deferred to a future occasion (Art. 81).

CHAPTER II.

Dilatation of Solids.

32. In the present chapter the relation between the temperature and the volume of a solid will be investigated.

It is a general, though not a universal law, that when such a body increases in temperature it also expands in volume, or dilates, and that when it diminishes in temperature its volume contracts, so that when restored to its original temperature it resumes its original volume.

The subjoined apparatus (Fig. 8) is used to illustrate the expansion of solids through heat. A rod *A* is fixed at one end by a screw *B*, while the other end presses against the

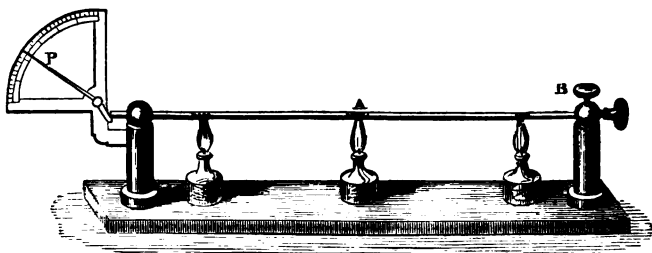


Fig. 8.

short arm of a lever, whose long arm *P* forms a pointer. This pointer exhibits by its movement along a graduated scale any change of length in the rod—thus, were the rod to expand, the pointer would be pushed upwards; and were it to contract, the pointer would fall downwards. Any small change in the length of the rod is by this means rendered visible.

But the way in which a solid expands is different according as the substance is crystalline in its structure or amorphous, and hence the subject naturally divides itself into two parts. In the first of these the expansion of uncrystallized solids will be considered, while in the second the behaviour of crystals under change of temperature will be shortly described.

DILATATION OF UNCRYSTALLIZED SOLIDS.

33. In some cases it is the increment of the volume of a body that we wish to estimate, while in others, as for instance when we are considering a substance, such as a bar, of which the length is the important element, it is change of length with which we concern ourselves. The

former of these is called *cubical* and the latter *linear* dilatation or expansion. We shall commence with linear expansion: but let us first define what is meant by 'the coefficient of expansion,' whether linear or cubical. The coefficient of expansion of a substance is the expansion for one degree of temperature of that quantity of the substance whose length or volume (as the case may be) was unity at a certain standard temperature, as for instance at the temperature of melting ice.

Thus if the length of a brass bar be unity at 32° Fahr., at 33° it will be 1.00001: hence .00001 is the coefficient of linear expansion of brass for 1° Fahr.

34. Linear dilatation. Lavoisier's method. Several methods of finding the linear dilatation of solids have been proposed. In one of these, namely that adopted by Lavoisier and Laplace, a telescope is placed upon a horizontal axis, as in Fig. 9. This axis carries a cross piece *AB* rigidly attached to it, and a bar (not shown in the figure) fixed at one end is forced to expand by means of heat, and to press with its free end against the cross piece. This pres-

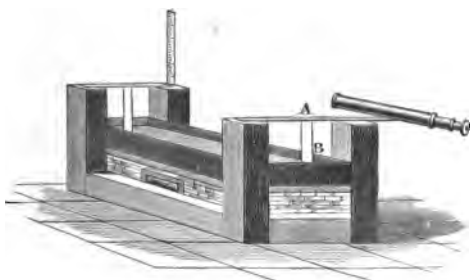


Fig. 9.

sure will move the cross piece and turn round the axis of the telescope to which the cross piece is rigidly attached, so that the telescope will now point to a different object. Suppose that the object to which it is pointing is a vertical scale of inches a considerable distance off. If a horizontal wire be placed in the telescope so as to appear in the centre

of its field of view, this will seem to have travelled over a great distance on the vertical scale for a very small expansion of the bar. It will be seen that this apparatus is similar to that of Fig. 8, the telescope and vertical scale of inches performing the part of the pointer and graduated quadrant.

35. Ramsden's method. In the apparatus of Roy and Ramsden there are three troughs, the first and the last containing iron bars, while the middle one contains the bar of which the dilatation is to be measured. To the two extremities of the iron bar contained in the first trough there are fixed the eye-pieces of two small telescopes, the object-glasses of which are fixed to the corresponding extremities

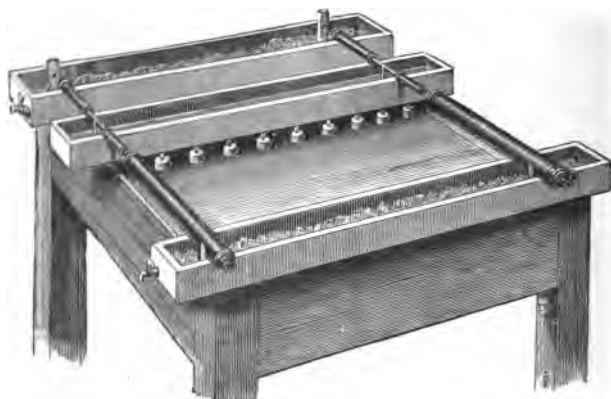


Fig. 10.

of the bar in the middle trough. These telescopes are directed towards two marks attached to the extremities of the iron bar in the farther trough. The first and third troughs are kept filled with melting ice, so that the iron bars in these are always of the same temperature. (These bars are permanently fixed at one end and moveable through

a collar at the other.) Hence the points of attachment of the eye-pieces of the two small telescopes to the first bar may be regarded as rigidly fixed, as well as the points of attachment of the two marks, which are fastened to the extremities of the iron bar in the third trough, inasmuch as there is no expansion or contraction of these two bars through change of temperature. On the other hand, the bar in the middle trough is first of all placed in ice, and afterwards in water, of which the temperature is varied by means of lamps, in order that the dilatation of this bar may be measured. This middle trough rests upon rollers, and by means of a screw attached to the table (not shown in the figure) the left-hand end of the bar is always kept in the same position, so that the object-glass of the left-hand telescope which is attached to the middle bar may be regarded as fixed. But the right-hand extremity of the middle bar, and consequently the object-glass attached to it, is moveable, and will move towards the right when an expansion takes place. At the left side therefore the eye-piece, object-glass, and mark are fixed, while at the right side the eye-piece and mark are fixed but the object-glass is moveable. Now the right-hand eye-piece has in its field of view a vertical thread, which at the beginning of the experiment, when all the three troughs are filled with melting ice, may be supposed to coincide precisely in position with the right-hand mark. But when the object-glass of this telescope has been moved owing to the expansion of the middle bar, this thread will no longer coincide with the mark: nevertheless it may be made to do so by means of a screw attached to the eye-piece and which moves the thread. It is thus apparent that the number of turns and fractional parts of a turn of this screw necessary to bring back the thread to coincidence with the mark affords the means of calculating the expansion of the

middle bar, which may thus be determined with very great precision.

36. Pouillet's and Daniell's methods. In the last method, as well as in that previously described, the bar of which the dilatation is to be measured is immersed in a liquid, and cannot therefore be heated to any very great extent. If we wish to measure the dilatation of a substance at a high temperature we must use some other method. Pouillet has devised an instrument by which the amount of dilatation may be measured at a distance, while Daniell has effected the same object in the following manner. The bar of which the expansion is to be measured is inserted into *A*, a black-lead tube, and pushed to the

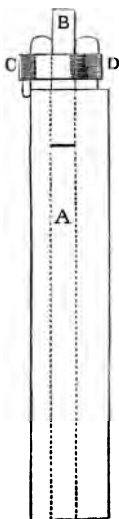


Fig. II.

bottom ; above it is placed an index *B*, which is pushed down into contact with the bar, and is kept somewhat tight by means of a collar *CD*. When the bar expands through heat this index is pushed up, but is left in its place when the same bar again contracts. Thus by an arrangement similar to that of the maximum thermometer the expansion of the bar may be determined. It may be easily shown that in this apparatus the index *B* (neglecting its contraction since it is small) will remain pushed out by a quantity which represents the difference between the expansion of the bar and of the tube containing it. For suppose that at the highest temperature reached the bar and the index *B* are in contact together.

As the temperature falls the bar will contract, leaving a vacant space between the bar and the index ; but, on the other hand, the whole tube as it contracts will tend to diminish this vacant space, and

to push the bar and the index nearer together. The vacant space will thus be the difference between the expansion of the tube and that of the bar, and indeed it is evident that if the bar be composed of the same material as the tube there will be no vacant space. In using Daniell's instrument it is therefore necessary to obtain independently the expansion of the tube.

37. The following table will exhibit the results obtained by these various instruments, and it is instructive to notice sometimes the coincidence between the determinations of different observers, and sometimes the difference between those of the same observer when operating upon different specimens of the same substance.

Table of linear dilatation of solids.

Name of substance.	Length at 100°C of a rod whose length at 0°C = 1.000000.	Name of observer.
Glass (tube without lead)	1.000876	Lavoisier and Laplace.
" "	1.000898	" "
" "	1.000918	" "
" (English flint) . .	1.000812	" "
" (French with lead) .	1.000872	" "
" (tube)	1.000776	Roy and Ramsden.
" (solid rod)	1.000808	" "
"	1.000861 ¹	Dulong and Petit.
" (3 parts sand, 2 lead, 1 alkali).	1.000729	Matthiessen.
Copper	1.001722	Lavoisier and Laplace.
"	1.001712	" "
"	1.001716	Daniell.
Brass	1.001867	Lavoisier and Laplace.
"	1.001890	" "
" (standard scale) . .	1.001855	Roy and Ramsden.
" (English plate in a rod 5 feet long) .	1.001893	" "
" (English plate in a trough of 5 feet) .	1.001895	" "

¹ Obtained from the cubical dilatation of these solids (see Art. 41).

Name of substance.	Length at 100°C of a rod whose length at 0°C = 1.000000	Name of observer.
Iron, soft (forged) . . .	1.001220	Lavoisier and Laplace.
" " (drawn) . . .	1.001235	" " "
" wrought . . .	1.001182 ¹	Dulong and Petit.
" . . .	1.001156	Borda.
Steel (untempered) . . .	1.001079	Lavoisier and Laplace.
" " . . .	1.001080	" "
" (tempered yellow) . .	1.001240	" "
" rod 5 feet . . .	1.001145	Roy and Ramsden.
Cast iron (prism length 5 feet) . . .	1.001109	" "
" " . . .	1.001072	Daniell.
Lead . . .	1.002848	Lavoisier and Laplace.
" . . .	1.002788	Daniell.
Tin (East Indies) . . .	1.001938	Lavoisier and Laplace.
" (Falmouth) . . .	1.002173	" "
" . . .	1.001767	Daniell.
Silver (fine) . . .	1.001910	Lavoisier and Laplace.
" (standard of Paris) . .	1.001909	" "
" . . .	1.001951	Daniell.
Gold (de départ) . . .	1.001466	Lavoisier and Laplace.
" (standard of Paris, not annealed) . . .	1.001552	" "
" (standard of Paris, annealed) . . .	1.001514	" "
" . . .	1.001230	Daniell.
Platinum . . .	1.000884 ¹	Dulong and Petit.
" . . .	1.000857	Borda.
" . . .	1.000902	Benoit.
Zinc . . .	1.002976	Daniell.

38. Remarks on the preceding table. If we suppose that by means of the methods already described a great amount of accuracy of measurement may be obtained, yet there is an uncertainty regarding the real temperature of the experimental bar, and this becomes very great for temperatures above the boiling-point of water. In such cases, where a bath is used, it is not only very difficult to keep this at a constant temperature, but it is also very difficult to estimate accurately the temperature by means

¹ Obtained from the cubical dilatation of these solids (see Art. 41).

of a thermometer. This uncertainty with regard to estimation applies still more strongly to higher temperatures. But for the range between freezing and boiling water, which is that of the above table, it may perhaps be assumed that the determinations are fairly correct. Whence then arise the differences between the results of different observers, and even between those of the same observer when estimating the dilatation of different specimens of the same substance? These are probably due to two causes. In the first place, substances which bear the same name are not always of precisely the same chemical composition. Of these, glass may be mentioned as a prominent example, and accordingly we find the dilatation of this substance ranging in the table from $\cdot000918$ to $\cdot000729$. Brass, cast iron, and steel are likewise compounds of which the composition is variable. But besides this, the commercial varieties of those substances which when pure are elementary, such as iron, lead, silver, gold, &c., often contain a very appreciable amount of impurity, so that the composition of different specimens is by no means uniform. In the second place, it ought to be observed that two solids may have precisely the same chemical composition, while yet their molecular condition may be different, owing to a difference in the treatment which they have experienced. Thus steel heated and suddenly cooled is a very different substance from steel which has not been treated in this manner; and accordingly we find that while steel tempered yellow has for its expansion $\cdot001240$, untempered steel has $\cdot001080$. Glass also will behave in a different manner according as it is annealed or unannealed, and in certain cases it is almost impossible to obtain two bars, although made of precisely the same material, which shall in all their properties be precisely alike.

39. Cubical dilatation of solids. To determine the

cubical dilatation of a solid we may either, first, weigh the substance at different temperatures in a liquid of which the absolute dilatation is known, or we may, secondly, enclose it in a glass vessel the remainder of which is filled with mercury or water; and if the absolute dilatation of either of these liquids is known, that of the glass envelope and of the enclosed solid may be easily determined. To illustrate this second method let us in the meantime regard the dilatation of mercury as known, and suppose that the following experiment has been made.

A glass bottle thoroughly cleansed, so as to admit of being well filled with mercury without air specks, is found to hold at 0°C 10169.3 grains of this fluid, while at 100°C it only holds 10011.4 grains. Now it is known from Regnault's experiments (see Art. 52) that the dilatation of mercury between 0° and $100^{\circ} = .018153$, that is to say, a quantity of this fluid occupying a volume equal to unity at 0° will at 100° occupy a volume $= 1.018153$. Hence the weight of mercury occupying a given volume at 100° will bear to that occupying the same volume at 0° the proportion of $1 : 1.018153$, and hence (had the bottle not dilated) the weight of mercury filling it at 100° would have been $\frac{10169.3}{1.018153} = 9988.0$ grains. But the glass envelope having expanded, the bottle holds 10011.4 grains, or 23.4 grains more than it would have held had there been no expansion. The volume of the expanded bottle will therefore bear to that of the same bottle at 0° the ratio of 10011.4 to 9988, or of 1.002344 to 1; and hence *the expansion of this bottle between 0° and 100° will be .002344.*

Let us now suppose that this bottle contains a piece of iron weighing 2000 grains, and that the remainder of it is filled with 6707.8 grains of mercury at 0° , while at 100° the mercury filling it weighs only 6599.4 grains. From this it

follows that the volume of the iron at 0° = vol. of 3461.5 grains of mercury at 0° , and also that the volume of the iron at 100° = vol. of 3412 grains of mercury at 100° = vol. of 3412×1.018153 grains of mercury at 0° .

Hence $\frac{3412 \times 1.018153}{3461.5} = 1 + \text{cubical dilatation of iron between } 0^{\circ} \text{ and } 100^{\circ} = 1.003593$.

Hence according to this experiment .003593 denotes the cubical dilatation of iron between 0° and 100°C^1 .

40. This example is sufficient to give an idea of the process employed, which may be used for such substances as do not act chemically upon mercury, and even for those metals which do so, provided that they are protected by a thin film of their oxide.

The following table exhibits the cubical dilatations obtained after this method by different observers; of these MM. Dulong and Petit, and also M. Regnault, employed mercury as their fluid, while, on the other hand, Kopp made use of a flask filled with water.

Table of cubical dilatation of solids.

Substance.	Mean coefficient of expansion for 1°C between 0°C and 100°C	Mean coefficient of expansion for 1°C between 0°C and 300°C	Observer.
Glass	.00002584	.00003039	Dulong and Petit
„ (ordinary)	.00002761	.00003056	Regnault
„ (crystal) . .	.0000228	.0000233	„
Copper	.00005155	.00005650	Dulong and Petit
„	.000051		Kopp
Iron	.00003546	.00004405	Dulong and Petit
Lead	.000089		Kopp
Tin	.000069		„
Zinc	.000089		„

¹ I am indebted for the above method of solving this example to Mr. C. Fessenden of Ontario.

Dr. Matthiessen has lately made a great number of very valuable experiments on the cubical dilatation of metals and alloys by means of weighing them in water at different temperatures.

The metals employed for these experiments were well purified and cast in a well-smoked mould which gave the casting the shape of a double wedge. Owing to the action of the water on some of the metals and alloys the castings had in some cases to be varnished or gilded, but it was proved that this had no influence on the results obtained. The apparatus and method of observation are described in Art. 54 of this volume.

By these means Dr. Matthiessen has obtained the following results.

Table of cubical dilatation of metals.

Name of metal.	Mean coefficient of expansion for 1°C between 0°C and 100°C.
Cadmium	.00009478
Zinc	.00008928
Lead	.00008399
Tin	.00006889
Silver	.00005831
Copper	.00004998
Gold	.00004411
Bismuth	.00003948
Palladium	.00003312
Antimony	.00003167
Platinum	.00002658

For alloys Matthiessen has obtained the following law :
The coefficients of cubical or linear expansion by heat of an alloy between 0° and 100°C are approximately equal to the mean coefficients of cubical or linear expansion by heat of the component metals.

He argues from this that the determinations of the expansion by heat of alloys give in general no indication as to their chemical nature, and that they differ in this respect from determinations of the electric conductivity of

alloys, by which he has found that we may gain an insight into their chemical nature, the observed conductivity being often greatly less than the nature of the components would lead us to expect.

Other substances besides those mentioned in the above table have engaged the attention of observers. M. Brunner (fils) has made experiments on the cubical dilatation of ice. His method consisted in determining the specific gravity of this substance at different temperatures. From these experiments he concludes that, while at 0°C ice has a density of 0.91800, at -19°C its density has increased to 0.92013. This would give a cubical dilatation for 1°C of .000122.

41. Remarks on the above tables. Relation of cubical to linear expansion. In comparing the former table of cubical dilatation with the preceding one of linear dilatation we obtain the following result.

Comparison of linear and cubical dilatations.

Substance.	Mean linear expansion between 0° and 100°C .	Observers.	Mean cubical expansion between 0° and 100°C .	Observers.
Glass . .	.000851	{ Lavoisier and Laplace, Roy and Ramsden. }	.00254	{ Dulong and Petit, Regnault. }
Copper . .	.001717	{ Lavoisier and Laplace, Daniell. }	.005127	{ Dulong and Petit, Kopp. }
Lead . .	.002818	{ Lavoisier and Laplace, Daniell. }	.0089	Kopp.
Tin . . .	.001959	{ Lavoisier and Laplace, Daniell. }	.0069	,,
Zinc . . .	.002976	{ Lavoisier and Daniell. }	.0089	,,
Iron . .	.001204	{ Lavoisier and Laplace, Borda. }	.003546	{ Dulong and Petit. }

From this it will be seen that the cubical expansion is in every case equal to about three times the linear expansion of the same substance. The reason of this relationship between the two follows at once from the fact that when an uncrystallized solid expands it does so in such a manner that its figure at one temperature is similar to that at another. Universal experience demonstrates the truth of this statement; and it can be very easily shown that assuming it to be correct the cubical dilatation of a substance will then be as nearly as possible three times as great as its linear dilatation.

For let a represent the coefficient of linear expansion, and a' that of cubical expansion of the same substance, for a rise of 1°C above 0° ; also let L and V represent the length and volume of the substance at 0° . Then $L(1+a)$ and $V(1+a')$ are its length and volume at 1° . But since similarity of figure is preserved, we shall have, by a well-known proposition in geometry,

$$\begin{aligned} V:V(1+a')::L^3:L^3(1+a)^3; \\ 1:1+a'::1:(1+a)^3; \\ \therefore 1+a'=(1+a)^3=1+3a+3a'+a^3. \end{aligned}$$

Now since a is a very small fraction we may dispense with the last two terms of the right-hand member of this equation, and hence $1+a'=1+3a$, or $a'=3a$ nearly; that is to say, the cubical is equal to three times the linear dilatation.

42. Increase of the coefficient of expansion with the temperature. It will be seen by comparing the mean coefficient of expansion between 0° and 100°C with that between 0° and 300°C , that the latter is greater than the former for each of the substances given in the table; it would appear, however, that in the case of hardened steel the coefficient of expansion diminishes as the temperature

increases; but this is probably due to the fact that heat deprives the steel of part of its temper, and that it thus becomes more like soft steel, which has a smaller coefficient of expansion than hard steel, as may be seen from the table of linear dilatation already given.

DILATATION OF CRYSTALS.

43. It is found that many crystals do not expand under heat equally in all directions so as to preserve their similarity of figure. Mitscherlich has investigated at great length the action of heat upon crystals, and has obtained the following laws:—

1. *Crystals of the regular system which do not cause double refraction dilate uniformly in all directions in the same manner as uncrystallized bodies.*

2. *Crystals that are optically uniaxal are differently affected by heat in the direction of the principal axis and in the direction of the three secondaries, but in the direction of the latter they are similarly affected.*

3. *Crystals that are optically biaxal dilate unequally in all directions.*

Mitscherlich believes he has determined, as the result of his investigations, that the tendency of heat in crystals is to increase the mutual distance of the molecules the most in that direction in which this distance is least, and thus to equalize the distances in different directions and bring the axes into a state of equality.

REMARKS ON THE DILATATION OF SOLIDS.

44. The general law connected with the dilatation of solids is that enunciated at the commencement of this chapter, which states that such bodies expand when heated, but recover their original volume when they are restored to their original temperature.

Neither of these statements is, however, universally true, and a singular exception to the first occurs in the case of Rose's fusible metal. Erman, and afterwards Kopp, have found that there is for this body in the solid state a point of maximum expansion through heat, after which, if the temperature be increased, it contracts instead of expanding. According to Kopp something of the same kind takes place in sulphur.

A still more remarkable exception was brought to light in some experiments made by Fizeau in 1866, from which it would appear that iodide of silver contracts by heat and expands by cold, the phenomenon being perfectly regular and continuous between -10° and $+70^{\circ}\text{C}$. This curious exception has been investigated by Mr. G. F. Rodwell (Proc. R. S. Dec. 1874), who has arrived at the following conclusions.

1. Iodide of silver exists in three allotropic forms, viz. (a) at temperatures between 116°C and its fusing-point, as a plastic, tenacious, amorphous substance possessing a reddish colour and transparent to light; (β) at temperatures below 116°C , as a brittle, opaque, greenish-grey, crystalline mass; and (γ) if fused and poured into cold water, as an amorphous, very brittle, yellow, opaque substance.

2. That the iodide possesses a point of maximum density at or about 116°C at the moment before passing from the amorphous into the crystalline condition.

3. That if we allow a mass of molten iodide to cool, the following effects may be observed:—(a) at the moment of solidification a very considerable contraction takes place; (β) the solid, on further cooling, undergoes slight and regular contraction after the manner of solid bodies in general, until (γ) at or about 116°C it undergoes sudden and violent expansion, passing from the amorphous into the crystalline condition; (δ) after undergoing this expan-

sion the mass on further cooling undergoes slight expansion, and (ϵ) the coefficient of contraction diminishes as the temperature decreases (or, otherwise expressed, the coefficient of contraction augments with the temperature).

45. In the second place, the statement regarding the recovery by a solid of its original volume when it resumes its original temperature is by no means absolutely correct. For if a solid be cooled very suddenly, in most cases its particles have not had time to bring themselves into the condition proper to the reduced temperature, and in consequence the substance is in a state of constraint, which continues often for a very long time. This is probably the cause of the change of zero in a mercurial thermometer (Art. 22). For when such an instrument is made, or filled, the bulb is heated and suddenly cooled, and hence its particles have not had time to approach so near to one another as they would have done had the process of cooling been very gradual. The bulb is therefore abnormally dilated, and only recovers from this state after a considerable time, during which a slow contraction takes place and the mercury is pushed up in the tube, or the zero appears to rise.

In like manner when such an instrument is exposed to the temperature of boiling water and suddenly cooled, the bulb remains somewhat dilated, or the zero appears to have fallen, and only recovers its former position after several weeks or months have elapsed.

Magnus, and afterwards Phipson, have noticed a similar behaviour in certain specimens of the idocrase and garnet family. These have their density considerably diminished after having been heated to a red heat, but in the course of time they recover their former volume.

Other instances of this behaviour might be mentioned, and the knowledge of the fact is of much importance in many of the arts. It is accordingly well known to workers

in the metals and in glass that the utensils which they form from the molten material require to be very carefully and slowly cooled in order that the particles may have time to assume their most stable position, otherwise the structure is fragile and comparatively useless. The process by which this is accomplished is called annealing.

It thus appears that time is an important element in the cooling of bodies ; and with this reservation it may not perhaps be erroneous to assert that a solid body heated and very slowly cooled will regain its original volume on regaining its original temperature.

CHAPTER III.

Dilatation of Liquids.

46. Apparent dilatation and real dilatation. The cubical dilatation of a liquid may be either apparent or real. By apparent dilatation is meant the apparent increase of volume of a liquid confined in a vessel which expands but in a less degree than the liquid which it contains. By real or absolute dilatation is meant the true change of volume of the liquid without reference to the containing vessel.

In order to find the real dilatation of liquids one of the following processes is employed.

47. (I) Method by thermometers. In this method the liquid under experiment is made to fill the bulb of a thermometer of which the internal volume or capacity is supposed to be known at the various temperatures of observation. This bulb is attached to a graduated stem,

and the internal capacity of each division of this stem is likewise supposed to be known.

When this instrument has been filled with the liquid under examination it is exposed to different temperatures, and for each of these the position which the extremity of the liquid occupies in the stem is accurately noted. It is clear that by this means the volume of the liquid for each temperature becomes known, and hence the amount of its dilatation may be easily deduced.

48. (II) Method by specific gravity bottle. Here a vessel, the internal volume of which is accurately known for all temperatures, is separately filled at each temperature with the liquid under examination, and the whole is then weighed. The weight of the vessel when empty is also ascertained, and thus the *weight* of liquid which it contains at each temperature becomes known. But the *volume* of this liquid is also known ; hence its density, which varies as the weight of unit of volume, becomes known, and thus the dilatation may be determined. In this method the kind of bottle generally used is one made of glass, having a glass stopper which fits it accurately. The stopper is ground out of a capillary tube, such as that used for the stem of a thermometer, and hence, when the bottle is filled with liquid and the stopper pushed home, any excess of liquid is forced out through the capillary orifice. The bottle ought to be filled in this manner at a temperature lower than that of observation, so that, when it is subjected to the higher temperature and the liquid expands the excess may escape by the orifice of the stopper and yet leave the bottle quite full.

49. (III) Method by weighing a solid in the liquid, or the areometric method. In this method a solid whose volume is accurately known for each temperature of observation is weighed while immersed in the liquid at these

temperatures. The difference between the weight of this solid in vacuo and its weight in the liquid will give us the means of determining the relative density of the latter at the various temperatures. This will be seen from the following example:—

Let us suppose that the volume of the solid at 0°C is denoted by unity, but at 100°C by 1.006. Suppose also that the apparent loss of weight of the solid when weighed in the liquid at 0° is 1800 grains, while at 100° the same is only 1750 grains: 1800 grains is therefore the weight at 0° of a volume of the liquid equal to unity, while 1750 grains is the weight at 100° of a volume of the liquid equal to 1.006. Hence 1739.56 grains will denote the weight of unity of volume of the liquid at 100° ; and hence also 1800 grains, which at 0° occupied a volume equal to unity, will at 100° occupy a volume

$$= \frac{1800}{1739.56} = 1.03474;$$

or the dilatation between these two temperatures is represented by .03474.

50. Absolute dilatation of mercury. In all these methods the capacity of the vessel or the volume of the solid employed must be known at the various temperatures of observation, or, in other words, we must know its cubical dilatation.

But the remarks in the preceding chapter (Art. 38) lead us to conclude that in order to determine accurately the cubical dilatation of a solid it is hardly sufficient to determine the linear dilatation of another specimen of the same material and to multiply this by three, but the cubical dilatation ought, if possible, to be obtained by direct experiment. We have already seen (Art. 39) that in order to accomplish this it is necessary to know the absolute dilatation of some one liquid, such as water or mercury.

The problem before us is thus reduced to the determination of the absolute expansion of some one liquid, after which that of other liquids may be easily derived. This therefore is a determination of much importance; and since mercury has been chosen for the purpose, we shall now proceed to show how the absolute expansion of this liquid may be found.

51. The method about to be described was first employed by MM. Dulong and Petit. It consists in filling a U-shaped tube with mercury, one limb being kept at a low and the other at a high temperature. The portion of the liquid which is heated will of course be specifically lighter than the other, and hence the hot column must be higher than the cold one, since the two balance each other hydrostatically. Thus if D, D' are the two densities, and H, H' the corresponding heights, we shall have $D : D' :: H' : H$, or the heights will vary inversely as the densities. This method is perfect in principle, but it is almost impossible to keep a column of mercury at a constant high temperature and at the same time be able to observe accurately the position of the top of the column. Regnault has however improved the apparatus so as to overcome this obstacle, and the following sketch will give an idea of the arrangement which he employed:— $ab, a'b'$ are the two vertical tubes to be filled with mercury, and these are connected together near the top by a horizontal tube aa' . At the bottom they are not connected together, but ab is connected with the horizontal tube bc , and $a'b'$ with $b'c'$. To the extremities of these horizontal tubes two vertical glass tubes $cg, c'g'$ are attached, and these are both connected with a tube hi leading to a large reservoir f supposed to be filled with gas whose temperature is constant; hence the pressure of this gas in the tubes $cg, c'g'$ is also constant. Heat is applied to the tube ab , and

by means of an agitator every part of this tube, including the mercury which it contains, may be brought to the same temperature throughout, and the value of this temperature is accurately ascertained. On the other hand, the tube $a'b'$ is exposed to a current of cold water of a known constant temperature.

The tubes ab , $a'b'$ are supposed to be filled with mercury

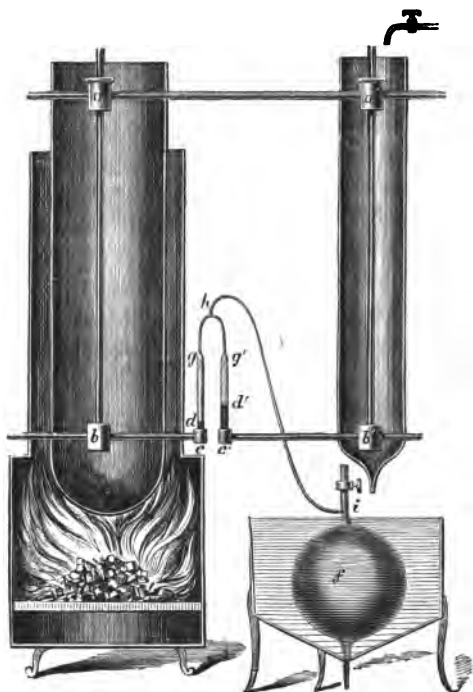


Fig. 12.

until above the level aa' , but we shall show in the sequel that it is not necessary to know the height of the fluid above this level.

Now let p denote the whole pressure due to the left-hand column of mercury, and p' the whole pressure due to the right-hand column. The pressure at c is evidently p , while that at c' is p' . Hence the pressure at $d = p$ - pressure of column cd , and in like manner pressure at $d' = p'$ - pressure of column $c'd'$. But the pressure at d is equal to that at d' , both being equal to the pressure of the gas in the reservoir f : hence we have

p - pressure of $cd = p'$ - pressure of $c'd'$,
and therefore

$$p' - p = \text{pressure of column } (c'd' - cd); \dots \quad (1)$$

that is to say, the difference between the pressures of the two great vertical columns is equal to the pressure of the column of mercury contained between the levels d' and d . Now since the tubes $ab, a'b'$ communicate together by aa' , it is evident from hydrostatical principles that the portions of the two vertical columns above a, a' are in equilibrium with each other, and therefore that the pressures of these two portions are equal. But p , or the whole pressure of the left-hand column, = pressure of column ab + pressure of portion above a ; and in like manner $p' =$ pressure of column $a'b'$ + pressure of portion above a' . Now since the pressures above a, a' are equal, it follows that

$$p' - p = \text{pressure of } a'b' - \text{pressure of } ab, \dots \quad (2)$$

and equating (1) with (2),

$$\text{pressure of } (c'd' - cd) = \text{pressure of } a'b' - \text{pressure of } ab.$$

We have thus obtained an expression for the difference in pressure between two columns of mercury ($ab, a'b'$) of equal length but of different temperatures, and since there is no occasion to view the top of the column, we can perfect our arrangements for keeping the whole at the same temperature throughout, while by the insertion of an air thermometer alongside of ab this temperature may be measured with great exactness. By this means therefore the relative

density of mercury at various temperatures may be determined, and its dilatation thence easily deduced¹.

52. Using this method, and also a modification of it, Regnault obtained results which enabled him to construct a table giving the dilatation of mercury for every ten degrees Centigrade from 0°C to 350° . But before exhibiting this table let us explain the distinction between the *mean* and the *true* coefficient of dilatation, as it is quite necessary to know this in the case of liquids which change their rate of expansion from one temperature to another.

In general language, if we take a quantity of liquid whose volume at 0°C is equal to unity, the mean coefficient of dilatation of the liquid for 1°C between 0° and any point is the mean rate of increase in volume of the liquid between these two points, that is to say, it is the whole expansion divided by the number of degrees included between the two points.

Thus we see in the following table, second column, that the whole dilatation of mercury between 0° and 100°C is $\cdot 018153$; that is to say, a volume of this fluid equal to unity at 0° will at 100° be equal to $1\cdot 018153$. Now $\cdot 018153$ is the increase for 100° , and hence the mean increase for 1° will be the hundredth part of this—or $\cdot 00018153$, which accordingly will be found in the third column opposite 100° , as denoting the mean coefficient of dilatation of mercury between 0° and that point.

On the other hand, the true coefficient of dilatation of the liquid at any point is the *rate of increase* in volume of the liquid at that point, as the temperature goes on *regularly increasing*.

¹ It has occurred to the writer of this treatise that it might be possible accurately to ascertain the length of the heated column in this experiment by means of an insulated metallic pointer that would allow an electric current to pass when it came into contact with the mercurial column.

It has been the general custom to refer this rate of increase to the original volume at zero, and the coefficient as so determined is given in the fourth column of the following table. For instance, the coefficient at 100° is found by this column to be $\cdot00018405$; that is to say, if the temperature rises through a very small distance such as 1° and becomes 101°C there will be an increase to the unit volume or volume which it had at zero represented by $\cdot00018405$. It has, however, been remarked by Pouillet and by Tait that this is not the proper way of representing the true coefficient, but that the rate of increase at 100° for 1° should have reference not to the volume at 0° but to the volume at 100° . Hence according to this definition the true coefficient at 100° will be $\frac{\cdot00018405}{1\cdot018153} = \cdot00018076$.

The fifth column of the following table exhibits these true coefficients ¹.

Table of the absolute dilatation of Mercury.

True temperature as determined by an air thermometer (<i>t</i>).	Whole dilatation from 0° to $t^{\circ}\text{C}$ of a volume of mercury equal to unity at 0° .	Mean coefficient of dilatation between 0° and $t^{\circ}\text{C}$.	Coefficient of dilatation at $t^{\circ}\text{C}$ referred to unit vol. at 0° .	True coefficient of dilatation at $t^{\circ}\text{C}$.
0			$\cdot00017905$	$\cdot00017905$
10	$\cdot001792$	$\cdot00017925$	$\cdot00017950$	$\cdot00017922$
20	$\cdot003590$	$\cdot00017951$	$\cdot00018001$	$\cdot00017938$
30	$\cdot005393$	$\cdot00017976$	$\cdot00018051$	$\cdot00017955$
40	$\cdot007201$	$\cdot00018002$	$\cdot00018102$	$\cdot00017972$
50	$\cdot009013$	$\cdot00018027$	$\cdot00018152$	$\cdot00017989$
60	$\cdot010831$	$\cdot00018052$	$\cdot00018203$	$\cdot00018006$
70	$\cdot012655$	$\cdot00018078$	$\cdot00018253$	$\cdot00018024$
80	$\cdot014482$	$\cdot00018102$	$\cdot00018304$	$\cdot00018041$
90	$\cdot016315$	$\cdot00018128$	$\cdot00018354$	$\cdot00018059$

¹ The accuracy of Regnault's determination of the absolute expansion of mercury has been confirmed by experiments very recently made by Dr. A. Matthiessen by a quite different method.

Table of the absolute dilatation of Mercury (continued).

True temperature as determined by an air thermometer (t).	Whole dilatation from 0° to $t^{\circ}\text{C}$ of a volume of mercury equal to unity at 0° .	Mean coefficient of dilatation between 0° and $t^{\circ}\text{C}$.	Coefficient of dilatation at $t^{\circ}\text{C}$ referred to unit vol. at 0° .	True coefficient of dilatation at $t^{\circ}\text{C}$.
100	.018153	.00018153	.00018405	.00018076
110	.019996	.00018178	.00018455	.00018092
120	.021844	.00018203	.00018505	.00018109
130	.023697	.00018228	.00018556	.00018125
140	.025555	.00018254	.00018606	.00018142
150	.027419	.00018279	.00018657	.00018159
160	.029287	.00018304	.00018707	.00018175
170	.031160	.00018329	.00018758	.00018190
180	.033039	.00018355	.00018808	.00018206
190	.034922	.00018380	.00018859	.00018221
200	.036811	.00018405	.00018909	.00018237
210	.038704	.00018430	.00018959	.00018252
220	.040603	.00018456	.00019010	.00018267
230	.042506	.00018481	.00019061	.00018282
240	.044415	.00018506	.00019111	.00018297
250	.046329	.00018531	.00019161	.00018313
260	.048247	.00018557	.00019212	.00018327
270	.050171	.00018582	.00019262	.00018341
280	.052100	.00018607	.00019313	.00018355
290	.054034	.00018632	.00019363	.00018370
300	.055973	.00018658	.00019413	.00018384
310	.057917	.00018683	.00019464	.00018398
320	.059866	.00018708	.00019515	.00018412
330	.061820	.00018733	.00019565	.00018426
340	.063778	.00018758	.00019616	.00018440
350	.065743	.00018784	.00019666	.00018453

It will be seen from this table that the true coefficient of dilatation of mercury increases with the temperature.

53. Dilatation of water. The determination of the dilatation of water is also a point of much importance; but before proceeding to this subject it will be necessary to notice a very striking peculiarity which this fluid exhibits with reference to its change of volume through heat.

If ice-cold water, or water at 0°C , be heated, it does not

at first expand as might be supposed, but contracts till about 4°C , and after that begins to expand. It thus exhibits a point of maximum density. This behaviour was illustrated by Hope by means of the following ingenious apparatus.

Fig. 13 represents a glass cylinder filled with water at an ordinary temperature, and having holes made for the insertion of two thermometers, one near the top and the other near the bottom. The middle of the cylinder is surrounded by an envelope filled with a freezing mixture. At first, as the temperature falls, the lower thermometer is very much affected, while the upper one falls but slowly. This continues until a temperature about 4°C is reached, when the lower thermometer ceases to fall, remaining stationary for some time. On the other hand, the upper one begins to fall more rapidly, and continues doing so until it reaches the freezing-point. This behaviour is explained by supposing that water attains a point of maximum density at about 4°C , below which it expands instead of contracting. At first therefore the particles of water contiguous to the freezing mixture becoming denser descend, and are replaced by warmer particles from beneath: and this process goes on until the water below *A* is reduced to 4°C ; while, on the other hand, that above the freezing mixture is not so cold. But as the action proceeds, the water contiguous to the freezing mixture having already attained its point of maximum density, becomes specifically lighter instead of heavier, and rising upwards rapidly cools the upper thermometer: all this while the lower thermometer remains stationary at the point which corresponds to the maximum



Fig. 13.

density of water. Many observers have made experiments with the view of determining the temperature corresponding to the maximum density of water, and by the mean of all their determinations this appears to be as nearly as possible equal to 4°C , or $39^{\circ}\cdot 2$ Fahr. Various watery solutions also possess their own points of maximum density; but a very extensive series of researches made by M. Pierre tends to show that for other liquids such points do not exist.

54. Having made these remarks on this peculiarity of water and watery solutions, let us now exhibit a table framed by M. Rosetti, in which the volume and density of water is given at the various temperatures from -10° to 100°C .

*Table of the Volume and Density of distilled Water
(the volume and density at 4° taken as unity).*

Temperature.	Volume.	Density.	Temperature.	Volume.	Density.
-10°	1.001858	.998145	14°	1.000701	.999299
-9	1.001575	.998427	15	1.000841	.999160
-8	1.001317	.998685	16	1.000999	.999002
-7	1.001089	.998911	17	1.001160	.998841
-6	1.000883	.999118	18	1.001348	.998654
-5	1.000702	.999298	19	1.001542	.998460
-4	1.000545	.999455	20	1.001744	.998259
-3	1.000410	.999590	21	1.001957	.998047
-2	1.000297	.999703	22	1.002177	.997826
-1	1.000203	.999797	23	1.002405	.997601
0	1.000129	.999871	24	1.002641	.997367
1	1.000072	.999928	25	1.002888	.997120
2	1.000031	.999969	26	1.003144	.996866
3	1.000009	.999991	27	1.003408	.996603
4	1.000000	1.000000	28	1.003682	.996331
5	1.000010	.999990	29	1.003965	.996051
6	1.000030	.999970	30	1.004253	.995765
7	1.000067	.999933	40	1.00770	.99235
8	1.000114	.999886	50	1.01195	.98820
9	1.000176	.999824	60	1.01691	.98338
10	1.000253	.999747	70	1.02256	.97794
11	1.000345	.999655	80	1.02887	.97194
12	1.000451	.999549	90	1.03567	.96556
13	1.000570	.999430	100	1.04312	.95865

The numbers in this table represent the means of the results of experiments made by Despretz (1837), Kopp (1847), Pierre (1852), Rosetti (1868), Hagen (1855), Matthiessen (1865), of whom the first four employed the method by thermometers (Art. 47), and the last two the areometric method, or that of weighing a solid in a liquid (Art. 49).

It may appear anomalous that this table should descend below the freezing-point of water, but we shall afterwards see (Art. 98) that this liquid, if kept perfectly still, may be brought to a lower temperature than its usual freezing-point without assuming a solid state.

Matthiessen's experiments.—It was remarked in Art. 50 that in the areometric method the cubical dilatation of the solid employed must be known at the various temperatures of observation. It was also remarked that in order to determine accurately the cubical dilatation of a solid it is hardly sufficient to determine the linear dilatation of another specimen of the same material and to multiply this by three, but the cubical dilatation ought, if possible, to be obtained by direct experiment. This, however, cannot be done unless we know the absolute dilatation of some one fluid such as water or mercury.

The uncertainty introduced into a determination of the expansion of water by the areometric method when we deduce the cubical expansion of an auxiliary solid from its linear expansion becomes, however, very small when the solid is one which has a very small coefficient of expansion compared with water. For this reason Matthiessen employed pieces of glass cut from rods of which in the first place he determined the linear expansion with great accuracy.

The method which he adopted for weighing accurately these pieces of glass in water of different temperatures is exhibited in Fig. 14. The piece of glass to be weighed was attached to the end of a fine platinum wire hung from

a balance-pan above. The hot-water box below was made of zinc, double sided and encased in wood. The covers were cut in two to allow them to be put on or taken off

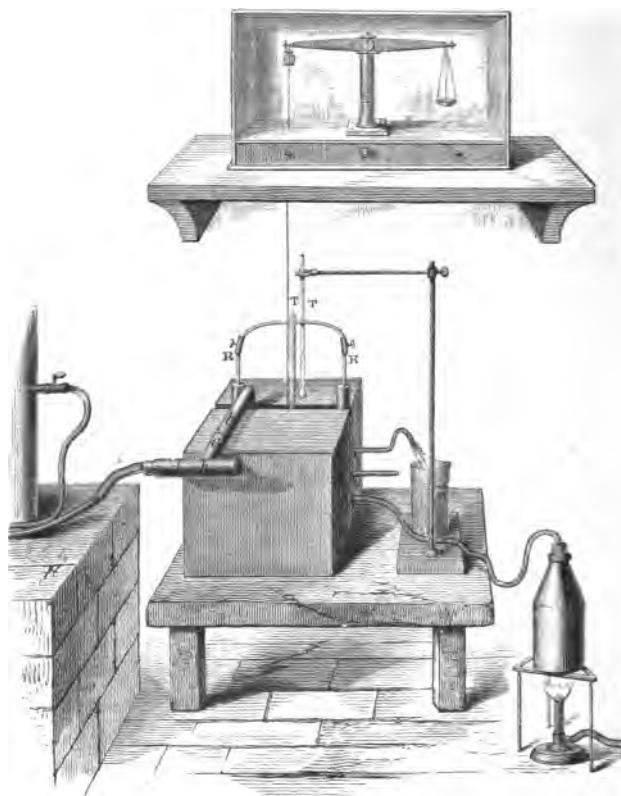


Fig. 14.

without disturbing the fine wire. The stirrer was a square piece of zinc soldered to the wires RR. A draft pipe leading into a chimney where gas was burning served to draw off the steam formed at high temperatures, thereby

preventing its condensation on the platinum wire. It was found by experiment that this draft had not the slightest influence on the weighings.

A silver cylinder filled with distilled water stood in the middle of the box, and in it the glass was weighed. The water in the box was heated by steam supplied by means of a small boiler heated by gas at some distance from the apparatus, and by carefully regulating the gas it was found that any temperature between 50° and 100°C might be kept constant for some time.

The following table exhibits some of the actual results obtained by the different experimenters, from which it will be seen that the determinations of Matthiessen and Despretz agree very well together.

Expansion of water according to different observers.

	Despretz.	Kopp.	Pierre.	Rosetti.	Hagen.	Matthiessen.
4°C	1.000000	1.000000	1.000000	1.000000	1.000000	1.000000
10	1.000268	1.000247	1.000271	1.000246	1.000269	1.000271
15	1.000875	1.000818	1.000850		1.000849	1.000892
20	1.001790	1.001690	1.001717	1.001742	1.001721	1.001814
30	1.004330	1.004187	1.004195		1.004250	1.004345
40	1.007730	1.007654	1.007636	1.007738	1.007711	1.007730
50	1.012050	1.011890	1.011939	1.011907	1.011994	1.011969
60	1.016980	1.016715	1.017243	1.016861	1.017009	1.016964
70	1.022550	1.022371	1.023064	1.022529	1.022675	1.022648
80	1.028850	1.028707	1.029486	1.028836	1.028932	1.028953
90	1.035660	1.035524	1.036421	1.035662	1.035715	1.035813
100	1.043150	1.043114	1.043777	1.043116	1.042969	1.043159

Perhaps the most exact determination of the density of water between 0° and 30°C has been recently made by M. Marek, whose results differ slightly from those given in Rosetti's Table.

Matthiessen also redetermined the coefficient of expansion of mercury by weighing it (enclosed in a bucket) in water of different temperatures. By this means he determined its mean coefficient of dilatation between 0° and 100°C to

be $\cdot 0001812$, a number closely agreeing with Regnault's, which was $\cdot 0001815$.

55. Dilatation of other liquids. The dilatations of a great many liquids have been carefully determined by M. I. Pierre, and he has embodied his results in expressions of the following kind—

$$\delta_t = at + bt^2 + ct^3;$$

where δ_t represents the dilatation of unit volume from 0° to $t^\circ\text{C}$, and where a, b, c are constants depending on the nature of the substance. This expression, he finds, generally represents the expansion of a liquid with considerable accuracy. We derive from his results the following table, in which the approximate temperature of the boiling-point of each liquid is compared with its coefficient of dilatation at 0°C .

Name of liquid.	Approximate temp. of boiling point in Centigrade degrees.	Coefficient of dilatation for 1°C at the temperature 0°C .
Chloride of ethyle	11.0	$\cdot 001575$
Oxide of ethyle (sulphuric ether)	35.5	$\cdot 001513$
Bromide of ethyle	40.7	$\cdot 001338$
Iodide of methyle	43.8	$\cdot 001200$
Sulphuret of carbon	47.9	$\cdot 001140$
Formiate of oxide of ethyle	52.9	$\cdot 001325$
Terchloride of silicon	59.0	$\cdot 001294$
Acetate of oxide of methyle	59.5	$\cdot 001296$
Bromine	63.0	$\cdot 001038$
Methylic alcohol	66.3	$\cdot 001186$
Iodide of ethyle	70.0	$\cdot 001142$
Acetate of oxide of ethyle	74.1	$\cdot 001258$
Alcohol	78.3	$\cdot 001049$
Terchloride of phosphorus	78.3	$\cdot 001129$
Butyrate of oxide of methyle	102.1	$\cdot 001240$
Bichloride of tin	115.4	$\cdot 001133$
Amylic alcohol	131.8	$\cdot 000890$
Terchloride of arsenic	133.8	$\cdot 000979$
Bichloride of titanium	136.0	$\cdot 000943$
Terbromide of silicon	153.4	$\cdot 000953$
Terbromide of phosphorus	175.3	$\cdot 000847$
Mercury (<i>Regnault</i>)	350.0	$\cdot 000179$

56. It will be gathered from this table that in general

liquids with high boiling-points expand less at the temperature 0°C than volatile liquids which boil at a low temperature, and it may be inferred that there is some connexion between the coefficient of expansion of a liquid and its volatility. This leads us to consider the dilatation of very volatile liquids.

57. Dilatation of volatile liquids. When we come to liquids, such as carbonic acid, which can only exist in this state at ordinary temperatures under very great pressure, we have reason to think that their coefficient of dilatation is extremely great. Thilorier in 1835 had made the curious remark that liquid carbonic acid presents the anomaly of a liquid more dilatable than any gas, and he concluded from his observations that its dilatation was four times greater than that of air. M. Drion has since made very careful experiments upon several volatile liquids, and among them liquid sulphurous acid and chloride of ethyle. From these he has constructed the following table.

True coefficient of expansion for 1°C .

Temperature.	Chloride of ethyle.	Sulphurous acid.	Temperature.	Chloride of ethyle.	Sulphurous acid.
0	.001482	.001734	70	.002390	.003176
10	.001588	.001878	80	.002625	.003608
20	.001699	.002029	90	.002910	.004147
30	.001811	.002192	100	.003250	.004859
40	.001919	.002371	110	.003690	.005919
50	.002045	.002585	120	.004306	.007565
60	.002202	.002846	130	.005031	.009571

We may perhaps conclude that the coefficient of expansion of a liquid is very great at those temperatures at which the substance can only exist in the liquid state under very great pressure.

58. Contraction of liquids from their boiling-points. Views perhaps analogous to those just mentioned induced

Gay-Lussac to compare the contraction of different liquids reckoned from their respective boiling-points, and he obtained the following results for alcohol and sulphuret of carbon.

Table of the contraction of alcohol and sulphuret of carbon for successive intervals of 5°C, reckoned from their boiling-points, the volumes at these points being equal to 1000.

Temperature interval.	Alcohol.	Sulphuret of carbon.	Temperature interval.	Alcohol.	Sulphuret of carbon.
5°	5.55	6.14	35°	40.28	40.48
10	11.43	12.01	40	45.68	45.77
15	17.51	17.98	45	50.85	51.08
20	24.34	23.80	50	56.02	56.28
25	29.15	29.65	55	61.01	61.14
30	34.74	35.06	60	65.96	66.21

It thus appears that the contractions of alcohol and sulphuret of carbon, reckoned in this way, are as nearly as possible the same. Pierre and Kopp have both verified this law of Gay-Lussac, and the former has shown—

1. That amylic, ethylic, and methylic alcohol follow nearly the same law of contraction, or, in other words, equal volumes of these liquids at their respective boiling-points will preserve their equality at all temperatures equidistant from these points.

2. That the same law holds true for the bromides and iodides of ethyle and methyle;

3. And in one or two other cases: but that in general two liquids formed by the combination of a common principle with two different isomorphous elements follow different laws of contraction starting from their respective boiling-points.

59. In conclusion, on comparing this chapter with the preceding we are led to the following result:—

1. *Solids have a much smaller coefficient of expansion than liquids.*

2. *The coefficient of expansion of liquids increases with the temperature.*

3. *The coefficient of expansion of a liquid which only preserves its state under very great pressure is probably very great.*

CHAPTER IV.

Dilatation of Gases.

60. BEFORE commencing the subject of this chapter the reader's attention must be drawn to the following experiment and law.

Let there be a tube shaped as in the accompanying figures, of a uniform bore throughout, and let it contain at the atmospheric pressure (equal, let us say, to 30 inches of mercury) a volume of air AB . If this air be shut out from the atmosphere by mercury, then the surfaces B and D of the mercury in the two limbs of the tube will be at the same level, since the

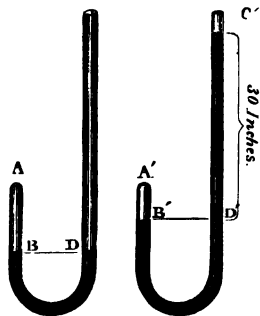


Fig. 15.

Fig. 16.

pressure upon the surface at B is supposed equal to that of the atmosphere pressing at D . Now if additional mercury be poured into the tube until there is a difference of 30 inches between the levels B' and C' , then it is evident that the air $A'B'$ exists under the

pressure of two atmospheres; for we have not only the column of mercury $C'D' = 30$ inches tending to press this air into less volume, but we have in addition the pressure of the atmosphere upon the surface C' , which is also equal to 30 inches of mercury. Hence we have the air in Fig. 16 existing at a pressure double of that in Fig. 15. Now it is an ascertained fact that the space occupied by the air in Fig. 16 will be one-half of that occupied by it in Fig. 15; and generally, *provided the temperature remains the same, the volume which a given mass of gas occupies is inversely proportional to the pressure under which it exists; or, in other words, its density is proportional to its pressure.* This law is known as that of Boyle or Marriotte.

61. But if the temperature be increased, the air will on this account alone tend to expand, and one of two things will happen. 1. If we wish to keep the air always occupying the same space we must employ additional pressure; 2. If we wish to keep it exerting the same pressure we must allow it to occupy additional space. Our subject thus naturally divides itself into two parts. In one of these we determine the relation between the pressure and temperature of a gas whose volume is constant, and in the other we determine the relation between the volume and temperature of a gas whose pressure is constant.

If we imagine Boyle's law to hold rigidly for gases, then the two cases are connected with each other in a very simple manner. For if a gas, whose volume is V and pressure P at 0°C , has at t° and under the same pressure the volume V' , then it is clear that were it constrained to occupy its old volume its pressure would be $P \times \frac{V'}{V}$.

Thus, whether we adhere to the method of constant pressures or to that of constant volumes we should in this case have precisely the same proportional change for

increase of temperature, this being in the one case *change of volume*, and in the other *change of pressure*; but it has been deemed right to determine the change by both methods, and we shall see in the sequel that the two values thus found are not precisely the same.

62. The fact of the dilatation of gas may be easily proved by filling a bladder nearly full of air, tying its orifice, and heating it; it will then soon appear to be quite full, the contained air having expanded by heat under the constant pressure of the atmosphere.

Dalton in this country and Gay-Lussac¹ in France were the first who investigated the law of expansion of gases with any considerable success, and they were both led to the conclusion that all gases expand equally for equal increments of temperature. With regard, however, to the precise law which connects together volume and temperature, there was a difference in the result obtained by these two philosophers. According to Gay-Lussac, the augmentation of volume which a gas receives when the temperature increases 1° is a certain fixed proportion of *its initial volume at 0°C* ; while according to Dalton, a gas at any temperature increases in volume for a rise of 1° by a constant fraction of *its volume at that temperature*.

Gay-Lussac's (or Charles') law may be expressed as follows.

Let V_0 , V_t denote the volumes at 0°C and t° of a certain quantity of gas existing at the pressure P , then these two volumes are connected with one another by means of the following formula—

$$V_t = V_0(1 + \alpha t);$$

where α is the coefficient of expansion, nearly the same for all gases, which it is the object of experiment to determine.

¹ Charles appears to have been the first to discover that the coefficient of dilatation is nearly the same in all permanent gases.

From this equation we derive at once the relation between the temperature and the density (density being represented by the mass contained in unit of volume) of air whose pressure remains constant. For let D denote the mass of air at the pressure P that occupies unit of volume at 0°C ; under the same pressure this mass will at t° occupy a volume equal to $1 + \alpha t$, and hence the mass of unit volume or the density at this temperature and pressure will be $\frac{D}{1 + \alpha t}$.

The dilatation of gases has since been investigated by Rudberg, Dulong and Petit, Magnus, and Regnault, and the result of their labours leaves little doubt that Gay-Lussac's method of expressing the law is much nearer the truth than Dalton's. It has also been ascertained that the coefficient of dilatation is not precisely, although very nearly, the same for all gases. The experiments of Regnault were conducted with very great care, and we shall now shortly describe, in the first place, his method of ascertaining the increase of pressure of a constant volume of air between 0°C and 100°C , and, in the second place, his method of ascertaining the increment of volume between the same limits of air of which the pressure remains constant.

63. Relation between pressure and temperature of air whose volume remains the same. The following description of an apparatus, nearly the same as Regnault's, and used by the author of this work for the same purpose, will enable the reader to understand the method pursued in this investigation.

A bulb b had its volume at 0°C and 100°C accurately determined by being gauged by mercury at these temperatures, as described in Art. 39; and the contained air had been thoroughly dried by being passed through a desiccating apparatus. The capillary termination of the bulb

was then attached to a tube T , connected with another tube T' which was open to the atmosphere.

The lower terminations of these tubes were fitted into a reservoir R containing mercury, and this reservoir might be enlarged or contracted at pleasure by means of a screw S which moved a piston out or in.

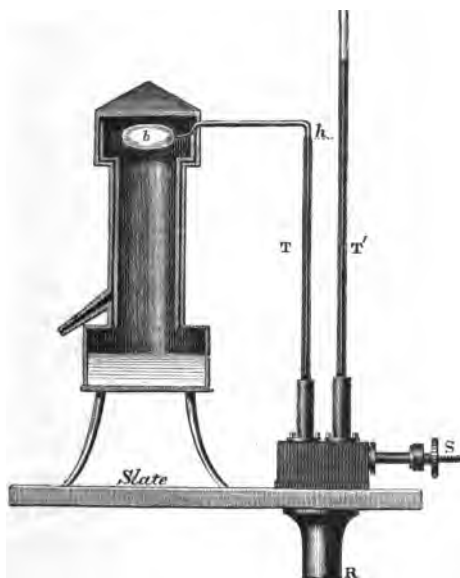


Fig. 17.

The whole apparatus was made to rest firmly on a slab of slate. The experiment consisted of two parts: the bulb b was first of all surrounded by melting ice, and by means of the screw S the mercury was forced to the height h in the tube T , and the difference of level between the surfaces of mercury in the two tubes was read by means of a cathetometer, which is an instrument for measuring vertical heights. Adding this to the height of the barometer, which

was observed at the same moment, the whole pressure under which the air in the bulb existed at the temperature of melting ice was thus ascertained. Let us call this P . The bulb b was next attached to a boiling-water apparatus, as in the figure, and by means of the screw S the mercury was forced up to the *same height* h in the tube T . Since the pressure of air increases with the temperature, it is evident that the pressure will now be greater, and that in consequence the mercury will be pushed high up in the tube T' . Taking the difference of level as before, noting the barometer, and adding the two heights together, we get the whole pressure under which the air now exists at the temperature of boiling water. Let this pressure be called P' . It is now very easy to construct the formula which must be applied.

Let the temperature of the surrounding atmosphere, as also that of the mercury in the tubes and reservoir, be $t^{\circ}\text{C}$; and let T° denote the temperature of boiling water at the present atmospheric pressure.

Further, let V denote the internal volume at 0°C of the bulb b and of that portion of the capillary tube which is subjected to the heating and cooling agents, and let v denote the internal volume at 0°C of that portion of the tube T above the mercury which is not subject to the influence of these agents, but which contains air having the temperature t .

Also let κ denote the coefficient of expansion for 1°C of the glass, and let α denote the corresponding coefficient of increase of pressure of dry air whose volume remains constant—this being what we wish to determine; and, finally, let us denote by D the mass of air which occupies unit volume under unit of pressure at the temperature 0°C .

Then DPV (according to Boyle's law) will denote the mass of that portion of the enclosed air existing in the

bulb (volume = V) at the temperature 0°C and under the pressure P when the bulb is surrounded by melting ice; also (Art. 62) $\frac{DPv(1+\kappa t)}{1+at}$ will denote the mass of that portion of the enclosed air existing at the same time in the tube (volume = $v(1+\kappa t)$) at the temperature of the atmosphere ($=t$) and pressure P . Hence the whole mass of enclosed air will be denoted by

$$DP\left\{V + \frac{v(1+\kappa t)}{1+at}\right\} \quad (1)$$

Now let the bulb be subjected to the temperature of boiling water ($=T$). The volume of the bulb then becomes $V(1+\kappa T)$, and hence the mass of air existing in the bulb at this temperature and under the pressure P' will be $\frac{DP'V(1+\kappa T)}{1+aT}$, while that existing in the tube (vol = $v(1+\kappa t)$) at the temperature of the atmosphere ($=t$) and pressure P' will be $\frac{DP'v(1+\kappa t)}{1+at}$.

Hence the whole mass of enclosed air will be denoted by

$$DP'\left\{\frac{V(1+\kappa T)}{1+aT} + \frac{v(1+\kappa t)}{1+at}\right\}. \quad (2)$$

But since the *mass* of air remains unchanged, being enclosed, we have (1) = (2); and hence, since D is a common factor,

$$P\left\{V + \frac{v(1+\kappa t)}{1+at}\right\} = P'\left\{\frac{V(1+\kappa T)}{1+aT} + \frac{v(1+\kappa t)}{1+at}\right\};$$

where everything is known but a , which may thus be easily determined. By a similar method Regnault found that if unity denote the pressure of a given volume of dry air at 0°C , its pressure at 100°C if confined to the same volume will be 1.3665. The author of this work has obtained a somewhat larger increase, but we may probably

assume the above number to represent the increased pressure of air of constant volume with great exactness.

64. Dilatation of air between 0°C and 100°C under constant pressure. A slight alteration in the apparatus of Fig. 17 enabled Regnault to make this determination. Here the air will of course expand and occupy part of the tube T , and it will therefore be necessary to surround the two tubes T, T' with water of a constant temperature, since nearly a fourth part of the enclosed air will exist in T , and its temperature must therefore be accurately known. By means of the screw S the mercury in the two tubes is brought as nearly as possible to the same level, both when the bulb is in melting ice and when it is in the boiling apparatus, so that in both these cases the pressure will be as nearly as possible equal to that of the atmosphere. Any small difference of level between the two tubes is read by means of a cathetometer, and the barometer is noted; so that the whole pressure under which the air exists in the two cases is accurately known; but these pressures will in this experiment be very nearly the same in both. By calibrating the tube the additional volume occupied by the air at the high temperature may be determined, and thus the coefficient of expansion becomes known.

From these and other experiments Regnault has concluded that while the dilatation of air between 0°C and 100°C is equal to $\cdot 3665$ of its volume at 0° when this dilatation is calculated by means of the law of Boyle from the change of *pressure* of air of which the *volume* is constant; yet when the dilatation is deduced directly from the change of *volume* while the *pressure* remains constant this coefficient is somewhat greater, viz. $\cdot 3670$.

Dividing these results by 180, we find the coefficient which denotes increase of *pressure* for 1° Fahr. of air whose *volume* is constant = $\cdot 002036$.

Also, the coefficient which denotes increase of *volume* for 1° Fahr. of air whose *pressure* is constant = .002039.

65. Dilatation of other gases at ordinary pressures. Regnault has investigated this subject minutely, and has found that different gases have notably different coefficients, and that the coefficient of the same gas differs according as it has been determined by the method of constant pressure or by that of constant volume. He gives the following results:—

Dilatation between 0°C and 100°C.

	Under constant pressure.	Under constant volume.
Hydrogen	0.3661	0.3667
Atmospheric air . .	0.3670	0.3665
Nitrogen		0.3668
Carbonic oxide . .	0.3669	0.3667
Carbonic acid . .	0.3710	0.3688
Protoxide of nitrogen	0.3719	0.3676
Sulphurous acid . .	0.3903	0.3845
Cyanogen	0.3877	0.3829

It will be noticed in this list that sulphurous acid and cyanogen, which have the greatest coefficients, are gases which may easily be liquefied; while, on the other hand, the three permanent gases, which have never been liquefied until very recently, and only with very great difficulty, have small coefficients.

66. Dilatation of gases existing under different pressures. The following law has been deduced by Regnault:—*‘Air and all gases except hydrogen have coefficients of dilatation which increase to some extent with their density.’*

Regnault has likewise enunciated the following very important law:—*‘The coefficients of dilatation of the different gases approach more nearly to equality as their pressures become feeble, in such a manner that the law which is expressed by saying that all gases have the same coefficient of*

dilatation ought strictly to be considered as a law which applies only to gas in a state of extreme tenuity, but which is departed from as gases become compressed, or, in other words, as their molecules approach each other.'

A gas whose molecules are so far apart as not to exert any sensible influence upon each other may be called a *perfect gas*.

67. Air Thermometer. We are now in a position to discuss the air thermometer, to which in our first chapter (Art. 14) we promised to return.

If we have a series of thermometers with different liquids, such as mercury, alcohol, water, &c., and all enclosed in envelopes of the same description, and if each instrument has been accurately pointed off and graduated in such a manner that 1°C denotes the one hundredth part of the capacity of the capillary tube between 0° and 100° , nevertheless these instruments, if plunged into the same liquid, will not all register precisely the same temperature.

But if we restrict our choice to thermometers with the same liquid, as, for instance, to mercurial thermometers made of the same kind of glass, we obtain instruments strictly comparable one with another, and these if plunged into the same liquid will all indicate the same temperature.

But though such instruments are comparable with each other, we are not yet sure if their common reading accurately represents the true temperature; for there is no obvious reason why we should prefer a mercurial to an alcohol or ether thermometer, which would both give slightly different indications. The mercurial thermometer stands therefore in the following position:—different instruments of this kind may be made to give identical indications, but yet we cannot rely upon these for accurately measuring temperature; nevertheless we cannot suppose that they are very far wrong.

Let us now employ a gas or air thermometer, and confine in envelopes of the same material different gases of sufficient tenuity and not liable to be easily condensed, and let us suppose that we have the means of ascertaining accurately the pressure which they exert upon their envelopes; and let us also in the meantime disregard the expansion of these envelopes. Now if all these gases have a common pressure at 0°C they will all have a common pressure at 100°C , or at any other temperature. If we make use of this pressure to determine the temperature, we have thus obtained different instruments whose indications are comparable with each other *even although the gases with which they are filled are different*. Gases, if of sufficient tenuity, are therefore in this respect superior to liquids; and it only now remains for us to determine the precise law which connects together the temperature and pressure of a gas in order to make a perfect thermometer. We have various reasons for imagining the law announced in Art. 62 to be correct, at least in the case of perfect gases. This law, taken in connexion with that of Boyle, asserts that if the pressure of a constant volume of gas be unity at 0°C and 1.3665 at 100°C , then the pressure at 50°C will be the mean between these two numbers, or 1.18325. Strictly speaking, it is impossible to prove this law experimentally with precision, for to do so implies the previous possession of an accurate instrument for measuring temperature. Now we have seen that the mercurial thermometer is not trustworthy, while for the purpose of this proof it must be presumed that the air thermometer does not yet exist, since in order to use it we must have a knowledge of this very law which we wish to prove. The case stands thus; if we employ mercurial thermometers (which we cannot imagine to be far wrong), this law is found to give a near approximation to the experimental result. There is, however,

a small difference, and the cause of this may be either that mercurial thermometers are not quite right, or that the law itself is only an approximate expression of the truth. Now, in the first place, we know very well that mercurial thermometers are not absolutely correct, and in the next place, with regard to the law, its extreme simplicity is in its favour, and we shall afterwards see that there are theoretical reasons for supposing it to be correct, at least for perfect gases.

In fine, we apprehend that a perfect gas obeys this law, and may be made to furnish us with a perfect thermometer, and if we cannot procure a gas that is quite perfect, yet atmospheric air deprived of moisture and carbonic acid is a substance sufficiently good for all practical purposes. A still better substance is hydrogen, for it follows Boyle's law more nearly and remains gaseous at temperatures well below those at which oxygen and nitrogen liquefy under the same circumstances of pressure.

The International Committee of Weights and Measures therefore adopted in 1887 as the normal thermometric scale that given by a constant-volume hydrogen thermometer wherein the gas is under the pressure of one metre of mercury when at the normal temperature of melting ice.

A comparison by M. Chappuis of the readings of a hydrogen thermometer with those of a mercury thermometer formed of French hard glass gives the following results:—

Mercury thermo- meter.	Hydrogen thermo- meter.	Mercury thermo- meter.	Hydrogen thermo- meter.	Mercury thermo- meter.	Hydrogen thermo- meter.
— 20	— 19.830	30	29.898	70	69.928
— 10	— 9.927	40	39.893	80	79.950
0	0.	50	49.897	90	89.974
10	9.948	60	59.910	100	100.
20	19.915				

The maximum difference between 0° and 100° is $\cdot 107$ and it occurs at $39^{\circ} \cdot 8$.

Although the air thermometer is in principle peculiarly fitted for the determination of very high temperatures, yet there are considerable mechanical difficulties in the employment of the instrument in such cases. Regnault invented in 1861 two modifications of this instrument in order to render it suitable to measure the temperature of furnaces. In one of these vapour of mercury is the gas employed, and the instrument is constructed as follows. There is a kind of flask, either cylindrical or spherical, which may be either of cast or wrought iron, of platinum or of porcelain: the mouth is closed by a plate containing a small aperture. From 15 to 20 grammes of mercury are added to this flask, which is then placed in that part of the furnace the temperature of which we desire to know. The mercury soon boils, its vapour expels the air by the orifice, and the excess of mercurial vapour goes off by the same means. When the apparatus has acquired the temperature of the furnace the flask is withdrawn and made to cool rapidly, and the mercury which remains in the flask is weighed. It may be weighed directly, or, if it contains impurity, it is dissolved in acid and estimated as a precipitate. This weight is that of the vapour of mercury which filled the flask at the temperature of the furnace, and the volume of the flask as well as the density of mercurial vapour being known this temperature may thus be determined.

In conclusion we append the results of a comparison made by M. Crafts between a hydrogen thermometer and a mercurial thermometer with an envelope of the glass called crystal :—

Mercury thermo- meter.	Hydrogen thermo- meter.	Mercury thermo- meter.	Hydrogen thermo- meter.	Mercury thermo- meter.	Hydrogen thermo- meter.
100	100.	180	180.34	260	259.61
110	110.02	190	190.32	270	269.50
120	120.04	200	200.27	280	279.37
130	130.09	210	210.18	290	289.12
140	140.16	220	220.08	300	298.79
150	150.25	230	229.98	310	308.40
160	160.33	240	239.86	320	317.97
170	170.35	250	249.74	330	327.52

M. Regnault found so great a difference as 4° between the indications of an air thermometer and a mercury thermometer with an envelope of crown glass in the neighbourhood of 35°C .

CHAPTER V.

Applications of the Laws of Dilatation.

68. Since all the bodies around us are subject to continual change of volume owing to their varying temperature, it is necessary to take account of this in very many operations and investigations whether of a scientific or strictly practical nature. Let us, in the first place, proceed to describe the influence which change of temperature exerts on our standards of length, mass, density and time.

STANDARDS OF LENGTH.

69. Supposing that a yard is taken to denote a certain absolute distance, and that the length of a bar is precisely one yard at the temperature 62°Fahr. , it is clear that, owing to the expansion of the material of the bar, its length will be

greater than a yard for temperatures higher than 62° , but less than a yard for temperatures below 62° .

If now we employ this bar as a standard by means of which to measure the absolute distance between any two points in terms of the yard as a unit of length, and if it be inconvenient or impossible to make this comparison at 62° Fahr., it will be necessary to know the precise temperature of our standard bar in order that we may know its real length.

The formation of a standard of length is an object of national importance, and we shall now shortly describe the respective standards authorized by the laws of England and France.

70. English Standard. The English standard of length was formerly the parliamentary standard yard executed by Bird in the year 1760. A yard was defined to be the straight line or distance between the centres of the two points in the gold studs in the brass rod formerly in the House of Commons, whereon the words 'Standard yard 1760' were engraved, the temperature of the standard being 62° Fahr.

On October 16, 1834, a fire occurred in the Houses of Parliament, in which the standards were destroyed. The bar of 1760 was recovered, but one of its gold pins having a point was melted out, and the bar was otherwise injured.

A committee was therefore formed to reproduce this standard yard in the best manner possible, and this was admirably accomplished chiefly through the labours of the late Mr. Sheepshanks. A new standard and four authorized copies were made and lodged at the office of the Exchequer, the Royal Mint, the Royal Society of London, the Royal Observatory, Greenwich, and the new palace at Westminster; and it was enacted (July 30, 1855), 'that the straight line or distance between the centres of the two

gold plugs in the bronze bar deposited in the office of the Exchequer shall be the genuine standard yard at 62° Fahr., and if lost it shall be replaced by means of its copies.' Many other copies of this standard have since been made, the errors of which have been very accurately ascertained.

When the length of a substance has to be measured with precision it is necessary to compare it either with the standard or one of its copies of which the error is known. It is here that the knowledge of the laws of dilatation becomes of importance, for to make the comparison accurately we must know

1. The precise temperature at which the comparison is made.
2. The coefficient of expansion of the standard used.

Suppose, for instance, that our standard is of brass, and that we are comparing with it a platinum scale at the temperature of 72° Fahr., and that we find the length of our scale to be 35.998 inches as read by the standard at this temperature; then in order to find the true length of our platinum scale at this temperature we must know the coefficient of expansion of the brass standard. Suppose this to be .00001 for 1° Fahr.; then if the standard is right at 62°, the true length of each of its apparent inches at 72° will be 1.0001 inch; and hence the true length of our platinum scale at the temperature 72° Fahr. will be $35.998 \times 1.0001 = 36.0016$ inches.

If we now wish to ascertain its length at 62°, we find, from the Table in Art. 37, the coefficient of dilatation for platinum for 1° Fahr. to be .0000049. Hence its length at 62° will be as nearly as possible $\frac{36.0016}{1.000049} = 35.9998$ inches. Thus we see that the two scales agree almost exactly at 62°, while they differ sensibly at 72° owing to the one scale being made of brass and the other of platinum.

71. French standard. The French standard of length is the mètre, which represents with considerable accuracy the 10,000,000th part of a quadrantal arc of a meridian on the earth's surface. The French standard platinum mètre made by Borda represents a mètre at 0°C, and all the copies of this standard are made so as to denote mètres and parts of a mètre at this temperature. One mètre is equal to 39·37043 English inches; that is to say, the length of the French standard platinum mètre at 32° Fahr., or 0°C, bears to the length of the English standard bronze yard at 62° Fahr. the proportion of 39·37043 : 36; but this will not be the proportion between these standards if compared together at any common temperature. The French standard is subdivided and multiplied according to the decimal scale, and the relation between our measures and those of France will be seen from the following tables:—

	In English inches.	In English feet = 12 inches.
Millimètre	·03937	·003281
Centimètre	·39370	·032809
Décimètre	3·93704	·328087
Mètre	39·37043	3·280869
Décamètre	393·7043	32·80869
Hectomètre	3937·043	328·0869
Kilomètre	39370·43	3280·869

In like manner we have

Centiare, or square mètre	=	10·76410	English square feet;
Are, or 100 square mètres	=	1076·410	" "
Hectare, or 10,000 square mètres	=	107641·0	" "

Also

Millilitre, or cubic centimètre	=	·06103	cubic inches;
Centilitre, or 10 cubic centimètres	=	·61025	" "
Decilitre, or 100 cubic centimètres	=	6·10254	" "
Litre, or cubic décimètre	=	61·02538	" "
Decalitre, or centistère	=	610·2538	" "
Hectolitre, or decistère	=	6102·538	" "
Kilolitre, or Stère, } or cubic mètre }	=	61025·38	" "

STANDARDS OF MASS.

72. These are sometimes termed standards of weight, but they are in reality standards of mass, in the comparison of which weight is made use of, since the weights of bodies at the same place of the earth's surface are proportional to their masses.

If all weighings could be made in vacuo, temperature would exercise no influence upon our measures of mass. But since weighings must be made in air, and since a substance weighed in air is apparently lighter than in vacuo by the weight of air which it displaces, and since the weight of a certain bulk of air of given pressure depends upon its temperature, it is necessary to know this temperature in very accurate determinations: the effect is however very small. The following are the standards of mass authorized by the laws of England and France.

73. *English standard.* Formerly in this country the standard of mass was the double pound Troy made by Mr. Bird, and it was resolved that the pound Troy should contain 5760 grains, and that 7000 such grains should make one pound avoirdupois. This standard was destroyed at the burning of the Houses of Parliament, but was restored in a very accurate manner by Professor W. H. Miller of Cambridge, with this difference, that whereas the old standard denoted one pound Troy, the new one represents one pound avoirdupois. Accordingly a standard and four authorized copies, all made of platinum, were constructed by this gentleman and deposited in the same places with the standard yard and its copies; and it was enacted, 'that the platinum weight deposited in the Exchequer shall be denominated the imperial standard pound avoirdupois, and that the $\frac{1}{7000}$ th of it shall be a grain, while 5760 such grains shall denote one pound Troy.'

74. French standard. In France the mass of a décimètre cubed of distilled water at the temperature of its greatest density (supposed equal to 4°C) is adopted as the standard of mass, and is called the Kilogramme, while the gramme is a centimètre cubed of distilled water at the same temperature *. The following table exhibits the relation between French and English measures of mass :—

	In English grains.
Milligramme.....	0.01543
Centigramme	0.15432
Décigramme	1.54323
Gramme	15.43235
Décagramme.....	154.32349
Hectogramme	1543.23487
Kilogramme	15432.34874

STANDARDS OF DENSITY.

75. In this country it was formerly the practice to determine the comparative density or specific gravity of solids and liquids by comparing them at 60° Fahr. with distilled water, also at 60° , reckoned as unity †, but the French practice is now generally adopted. For gases also the practice was usually stated to be a comparison at 60° with dry air under a barometric pressure of 30 inches of mercury at 60° , but here also the French system has been adopted.

In France the comparative density or specific gravity of solid and liquid bodies is determined with reference to that of water at its point of maximum density (supposed to be 4°C), and the comparison is always made at 0°C . Gases, again, are compared at 0°C with dry air at 0°C under the

* It will thus be noticed that considerations of temperature enter into the fundamental conception of the French standard of mass, and in so far it is different from the English pound, which is merely an arbitrary standard. We shall afterwards take occasion to make some remarks on the comparative merits of the French and English systems.

† A cubic inch of distilled water, in vacuo at 60° Fahr. opposed to weights also in vacuo, weighs 252.769 grains.

barometric pressure of 760 millimètres of mercury reduced to 0°C . The following examples will exhibit the effect of temperature upon determinations of density.

Example I.—It has been determined from Regnault's experiments that the mass of a litre of dry air at 0°C , and under the reduced pressure of 760 millimètres of mercury at Paris, is 1.29320 gramme; find what is the mass at London of 100 cubic inches of dry air at 60°Fahr. and 30 inches barometric pressure of mercury reduced to 60°Fahr. Now a litre is equal to 61.02538 cubic inches (Art. 71); also we have already seen (Art. 21) that 760 millimètres of pressure in Paris are equal to 29.913 inches in London at 32°Fahr. , while (by the table of Art. 52) we find that 29.913 inches of mercury at 32° are equivalent in weight to $29.913 \times 1.00279 = 29.997$ inches of mercury at 60°Fahr. or $15^{\circ}.5\text{C}$. Also 1.2932 gramme is equal to 19.9571 grains (Art. 74), and finally the comparative densities of gas existing under the same pressure at 32° and at 60° will be (Art. 64) in the ratio of

$$(1 + 28 \times .002039) : 1 \text{ or of } 1.0571 : 1.$$

Hence the required mass will be—

$$19.9571 \times \frac{100}{61.02538} \times \frac{30}{29.997} \times \frac{1}{1.0571} = 30.940 \text{ grains;}$$

where the first factor is on account of the difference of capacity of the two measures, the second on account of the difference of pressure, and the third on account of the difference of temperature.

Example II.—It has been determined at the Kew Observatory that the mass in vacuo at 62°Fahr. of a given volume of purified mercury is to that of the same volume of water in the proportion of 13590.86 to 1001.62 grains; what is the specific gravity of mercury at 0°C according to the French method of computation? We find by the

table of the absolute dilatation of mercury (Art. 52) that a unit of volume of this liquid at 0°C will become 1.00299 at 62°Fahr. , or $16^{\circ}\cdot6\text{C}$. Hence the mass of the above volume of mercury would at 0°C be $13590\cdot86 \times 1\cdot00299 = 13631\cdot497$ grains.

In like manner we find by the table of dilatation of water (Art. 54) that a volume of this fluid equal to unity at 4°C will at $16^{\circ}\cdot6\text{C}$ be 1.001115.

Hence the mass of the above volume of water would at 4°C be—

$$1001\cdot62 \times 1\cdot001115 = 1002\cdot737 \text{ grains;}$$

and hence the specific gravity of mercury according to the French method will be—

$$\frac{13631\cdot497}{1002\cdot737} = 13\cdot594 :$$

a determination by Regnault gives 13.596.

REMARKS ON THE ENGLISH AND FRENCH SYSTEMS OF STANDARDS.

76. The English standards of length and mass are arbitrary; that is to say, a yard and a pound do not bear any recognized relation to any natural constant.

On the other hand, the French chose their standard of length, or *mètre*, as that distance which was supposed to represent the ten millionth part of a quadrantal arc of a meridian of the earth's surface, while their standard of mass, or *kilogramme*, professed to be the mass of a *déci-mètre* cubed of distilled water at the temperature 4°C . On these principles Borda constructed the platinum *mètre* and the platinum *kilogramme*, which have become the authorized standards of France.

But whatever be the conception on which these standards

were originally founded, it is evident *that when once made and authorized they may to all intents be regarded as arbitrary standards.* For, though more accurate investigations have determined that one ten millionth of the earth's quadrantal arc is not exactly Borda's mètre, and that a décimètre cubed of distilled water at 4°C is not exactly Borda's kilogramme, the French nation still adhere to Borda's platinum mètre and kilogramme as their standards; and were these standards destroyed, it is probable that they could best be replaced by means of copies.

Nevertheless it is of importance to connect the authorized standards of a nation, always bearing in mind that they are in practice arbitrary, with certain natural constants supposed to be invariable: thus, for instance, to connect the standard of length with the length of a pendulum vibrating seconds, or with an arc of a meridian, and also to connect the standard of mass with that of length, after the manner of the French.

For it may be inferred from what we have said in Art. 45, that a standard of length, however carefully constructed and well annealed, may possibly in the course of time alter its length to a small but yet an appreciable extent.

But we cannot perhaps so readily suppose that any such change can take place in the length of the seconds pendulum or in that of any arc of the meridian, and hence any change in the length of the standard, if such occurred, might be detected by occasional comparisons with these natural constants.

In like manner a standard mass might ultimately become altered by slight abrasion of particles through frequent use, and it would therefore be of importance to connect it from time to time with the standard of length.

Another safeguard might be the construction of a standard

made of granite or marble, or of some substance which has probably become cooled by a very slow natural process, and which may therefore be supposed to be thoroughly annealed.

We remark, in conclusion, that the French system has some obvious advantages. In the first place, their standards of length and mass are divided and multiplied in accordance with the decimal system, by which means calculation is greatly simplified. Secondly, the mètre becomes their standard of length at 0°C , which is the most convenient temperature. Again, although the kilogramme may not exactly denote the mass of a cubic décimètre of distilled water at 4°C , yet it does so very nearly, and hence the French chemist, when he knows the specific gravity of any substance, knows also the mass of one cubic décimètre of that substance. For instance, if a substance have the specific gravity 2.5 at 0°C , it means that a cubic décimètre of that substance will at the temperature of 0°C weigh 2.5 kilogrammes.

On this and other accounts, the French or metrical system of weights and measures is very widely adopted by scientific chemists.

EFFECT OF TEMPERATURE UPON MEASURES OF TIME.

77. The rate of a clock depends upon the time in which its pendulum vibrates, and that of a watch upon the time of oscillation of its balance-wheel. Now the time of vibration of a pendulum depends upon its length; and since change of temperature alters the length of a pendulum, it likewise alters its time of vibration, the general effect being that the higher the temperature the longer does the pendulum become and the more slowly does it vibrate. In like manner a change of temperature, by altering the dimensions of the balance-wheel of a watch

and the elasticity of the spring, will alter its time of oscillation in such a manner that it will vibrate more slowly in hot weather than in cold.

All good clock-makers endeavour to obviate these sources of error by means of certain compensations which we shall now describe.



Fig. 18.

78. Graham's mercurial pendulum. The first who attempted to compensate for change of length of a pendulum was Mr. Graham, an English clock-maker. The rod of his pendulum, Fig. 18, was made of glass, to the lower extremity of which was attached a cylindrical vessel containing mercury. As the glass rod expands by heat the distance between the bottom of the vessel which contains the mercury and the point of suspension becomes greater; but since the column of mercury resting on this base expands upwards its centre of gravity is raised, or brought nearer the point of suspension. The effect of the lowering of the centre of oscillation due to the expansion of the glass may thus be counteracted by the rise of the same due to the expansion of the mercury. The correction for imperfect compensation is made by raising or lowering the cylinder of mercury by means of a screw.

79. Harrison's gridiron pendulum. Shortly after Graham, Mr. Harrison invented the arrangement in Fig. 19, which from its form is called the gridiron pendulum. The dark lines represent iron rods, the light lines brass or zinc; and it is evident that the former, being attached to the upper cross-pieces, will expand downwards, while the latter, being attached to the lower cross-pieces, will expand upwards. Hence the change of position of the bob due to a change of temperature will be denoted by the difference between the upward and the downward expansions. Let L

be the length of iron expanding downwards, and κ its coefficient of expansion ; also let L' denote the length of the other metal expanding upwards, and let κ' be its coefficient of expansion ; then if $L\kappa - L'\kappa' = 0$ it is evident that the position of the bob will remain unaltered, even though the temperature change.

The correction for timing the pendulum is made by the screw d , while that for imperfect compensation is effected by shifting one of the cross traverses.

In some respects this pendulum is better than the mercurial one, for should any cause render the bob of the latter somewhat warmer or colder than the rest of the pendulum, it is evident that this would produce its full effect upon the mercury, while the length of the pendulum rod would be little altered. The gridiron pendulum, on the other hand, is not liable to this imperfection. But here, as in other things, it is better to avoid the source of error than to trust too much to the perfection of the compensating arrangement ; and some astronomers, in order to procure the greatest possible regularity in their clock-rates, have removed the clocks themselves to a place where the change of temperature is extremely small.

80. Compensation balance for chronometers. If a straight ribbon or bar be made of two metals of different expansibility firmly attached to one another, and if the temperature rise, then one of these metals will expand more than the other. Under these circumstances the ribbon will bend so that the more expansible metal will form the outside or convex surface of the curve, and the less expansible

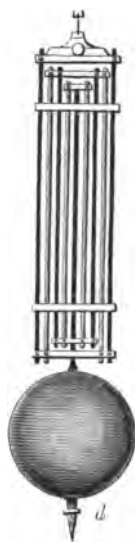


Fig. 19.

the concave. In like manner should the temperature fall the more expansible will form the inner or concave surface.

Now if the balance-wheel of a chronometer be formed as in Figure 20¹, not with one continuous rim, but with

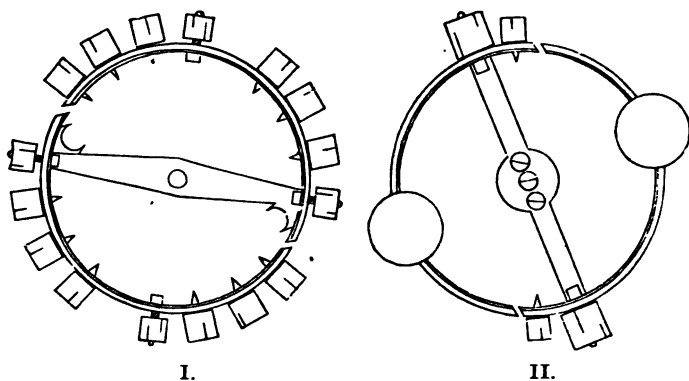


Fig. 20.

a broken rim of several separate pieces, all of which are fixed at one end and free at the other, the free ends being loaded; and further, if each piece be composed of two metals, of which the more expansible is placed outside; then it is evident, from what we have just said, that on a rise of temperature the loaded ends will approach the centre. This may be so arranged as to counteract the effect produced on the rate of the chronometer by the matter of the wheel being thrown from the centre on account of the radius being lengthened through expansion. In practice, however, this method of compensation is very seldom perfect, and the rate of the best chronometer probably varies a little from one temperature to another. In the Greenwich and Liverpool Observatories the tem-

¹ For the diagram of this figure I am indebted to the secretary of the Horological Institute.

perature corrections of chronometers are ascertained; and Mr. Hartnup, late of the Liverpool Observatory, has given some very interesting examples of his method of applying a temperature correction to these instruments.

OTHER APPLICATIONS OF THE LAWS OF DILATATION.

81. Bréguet's metallic thermometer. A very sensitive thermometer has been made by M. Bréguet on the principle just mentioned. It consists of a spiral (Fig. 21) composed of silver, gold, and platinum rolled together so as to form a very fine ribbon. In this state it is sensitive to an exceedingly small change of temperature, becoming coiled or uncoiled, owing to the different expansion of the metals of which the compound ribbon is made. A needle attached to one extremity of the coil points to a scale which is graduated experimentally by the aid of an ordinary thermometer.

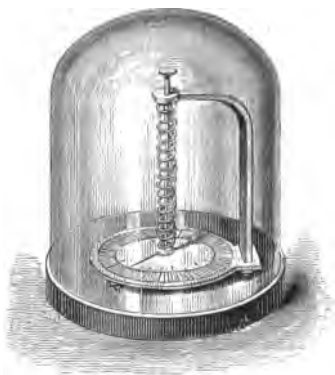


Fig. 21.

82. Reduction of barometric column. When the pressure of the atmosphere is expressed in the number of inches of mercury which it is capable of supporting, in order to render the statement complete it is necessary to know the temperature of the mercury, since this fluid has a different density at different temperatures. Thus we find (Art. 52) that one inch of mercury at 0°C will denote the same atmospheric pressure as 1.005393 inches at 30°C .

Another thing to be noted is that the scale, by aid of

which we read the column of mercury, even if correct, only denotes true inches and parts of an inch at 62°Fahr. , if it be of English construction, so that at any other temperature allowance must be made not only for the change in density of the mercury but for the change in length of the divisions of the scale.

Example.—Suppose that an English barometer with a brass scale, correctly graduated, reads 30 inches at 45°Fahr. , what is the pressure in true inches of mercury reduced to its specific gravity at 32°Fahr. ?

Since the scale is only correct (Art. 70) at 62°Fahr. , and since brass expands very nearly $\cdot 00001$ for 1°Fahr. , it follows that 30 apparent inches at $45^{\circ}\text{Fahr.} = \frac{30}{1\cdot 00017} = 29\cdot 995$ true inches. Also the density of mercury at 32°Fahr. (or 0°C) is to its density at 45°Fahr. (or $7^{\circ}\cdot 2\text{C}$) as $1\cdot 001294$ to 1. Hence the atmospheric pressure in mercury at 32°Fahr. will be $\frac{29\cdot 995}{1\cdot 001294} = 29\cdot 956$ inches.

In French barometers, on the other hand, the indications of the scale are correct at 0°C , the same temperature to which the mercurial column is reduced, while the scale itself represents millimètres.

In comparing an English and a French barometer it is therefore necessary to reduce the indications of each to 32°Fahr. ; that is to say, to find by the one the pressure of the air in inches of mercury at 32°Fahr. , and by the other the same in millimètres of mercury at 0°C . If both instruments are correct, their indications should then bear to one another the same ratio as a millimètre to an inch.

83. Expansion and contraction of metals. It requires the application of very intense pressure to produce the same change of volume in a solid or liquid body as that which is occasioned by a very small change of temperature.

It follows from this that the forces exerted by solids in contracting or expanding, and by liquids in expanding, must be very great. If a strong vessel be entirely filled with a liquid and then sealed tightly, the vessel will burst if there be a considerable rise of temperature.

In like manner it has been calculated, that a bar of wrought iron whose temperature is 15° Fahr. above that of the surrounding medium, if tightly secured at its extremities, will draw these together with a force of one ton weight for each square inch of section on cooling down to the surrounding temperature.

This property was first made use of in Italy to pull together walls which had bulged outwards. Iron bars were placed across the building and secured when in a heated state to the walls. As the iron cooled it contracted and the walls were thereby pulled together.

The same device was afterwards practised in Paris, and also in Ireland when repairing the cathedral at Armagh.

As another instance of the advantage which may be derived from the force of contraction, we may mention the familiar method by which tires are secured on wheels;—the tire is put on hot, when it fits loosely, but on its contraction in cooling it grasps the wheel with great force.

In all the arts it is of great importance to bear in mind the intensity of this force, sometimes with the view of guarding against its action, and sometimes in order to make it useful. Thus bars of furnaces must not be fitted tightly at their extremities, but must at least be free at one end. In making railways also a small space must be left between the successive rails.

Allowance must also be made for expansion and contraction in the case of tubular and lattice bridges. The reader who has visited the Menai tubular bridge will have observed the telescopic arrangement made for this purpose.

For a similar reason water or gas pipes are fitted to each other by telescopic joints; and, generally speaking, the effects which may follow change of temperature must always be taken into account by the constructor or engineer.

It is probably owing to the sudden change of volume from rapid cooling that tempered steel acquires that hardness which renders it so invaluable in the arts.

CHAPTER VI.

Change of State.—Liquefaction and Solidification.

84. Very many of the substances with which we are acquainted may be made to appear before us either in the solid, the liquid, or the gaseous condition; but there are others that can only be compelled to do so with very great difficulty.

Heat is the well-known agent which causes change of state; and it always acts in such a manner that a substance passes from the solid to the liquid, and from the liquid to the gaseous state, by the addition of heat, and back again in the reverse direction by the withdrawal of this agent. This law is quite universal, and the order is never reversed; so that, although we cannot as yet solidify alcohol, we are quite sure that our only chance of success lies in abstracting heat from this liquid; and in like manner, although we have not as yet succeeded in melting some substances, we are sure that if we ever succeed it will be by the application of great heat.

85. Let us in the first place study the passage of bodies from the solid to the liquid state.

The characteristics of these states are too well known to need lengthened description. We are all acquainted with the rigidity and permanence of form of a solid, and with the excessive mobility of a liquid which enables it readily to assume the form of the vessel in which it is placed; nevertheless, although nothing is more marked than the difference between the characteristic properties of solidity and liquidity, there is a set of bodies that possess properties intermediate to those of these two states, and receive the name of viscous bodies. Treacle is a body of this kind.

86. If a substance be capable of assuming the viscous state, we find that it does so before it begins to melt, and that it passes gradually from a solid state through a semi-solid viscous state to that of a liquid of evident mobility. Sealing-wax is a very good example of a substance of this nature; when cold it is brittle, when heated it first of all grows plastic and finally melts. In like manner, before fluidity iron loses its hardness and becomes soft to such an extent that pieces may be easily welded together or moulded into any form; and this property of iron greatly enhances its value in the arts. Other substances might be mentioned, and a gradual passage from the solid to the liquid state characterizes a large number of bodies. Furthermore, certain substances even after they have become unmistakably solid acquire certain properties, such as hardness and brittleness, in greater degree as the temperature continues to fall. Indeed, most of our hard bodies have high melting points, and the diamond, which is the hardest, is not susceptible of fusion at even the highest temperature hitherto obtained.

With many substances, however, the change from the solid to the liquid state is very abrupt, and such substances afford the means of indicating with very great precision, by their altered appearance, the attainment of certain

temperatures. Thus the temperature at which ice begins to melt is, under ordinary circumstances, a constant point, and is so used in the construction of thermometers.

87. But while there is a marked difference between bodies as to the abruptness with which they change their state, there is also a class of substances which change their composition in the act of changing their state. Such are saline solutions. In many of these a greater quantity of salt is retained in solution at a high temperature than at a low one, so that, when they are left to cool, crystals of salt are deposited.

With weak saline solutions, such as sea water, we have however a phænomenon of a somewhat different nature when the temperature is lowered. At a certain point which is constant for a solution of the same strength, the water solidifies as nearly pure ice, leaving the salt behind.

In what follows we shall distinguish between those substances which do not, and those which do, change their composition in changing their state. Also, our remarks must be taken as referring to substances in which the passage from the one state to the other is not gradual but abrupt.

PASSAGE FROM THE SOLID TO THE LIQUID STATE,
OR LIQUEFACTION.

88. **Fusion.** Substances which do not change their composition in passing from the solid to the liquid state. The following laws are observed by all such when melting.

1. *Each substance begins to melt at a certain temperature, which is constant for the same substance if the pressure be constant.*
2. *The temperature of the solid remains at this constant*

point from the time when fusion commences until it is complete.

3. If a substance expands in congelation its melting point is lowered by increase of pressure, but if a substance contracts in congelation its melting point is raised by increase of pressure.

89. The following table contains the melting points of various substances under the ordinary atmospheric pressure.

Table of melting points.

Name of substance	Temp. of melting point		Observer
	Fahr.	Cent.	
Mercury	-37.9	-38.8	Stewart.
Oil of vitriol	-30	-34.4	Regnault.
Bromine	+ 9.5	-12.5	Pierre.
Ice	32	0.0	
Phosphorus	111.5	44.2	Schrötter.
Potassium	136	57.8	Regnault.
Sodium	207.7	97.9	"
Sulphur	239	115.0	Person.
Tin	451	232.8	"
Bismuth	512	266.7	"
Lead	620	326.7	"
Zinc	680	360	Pouillet.
Antimony	810	432	"
Aluminium	1157	625	Le Chatelier.
Silver (pure)	1749	954	Violle.
Gold (pure)	1895	1035	"
Copper	1929	1054	"
Palladium	2732	1500	"
French wrought iron	2732	1500	Pouillet.
English wrought iron	2912	1600	"
Platinum	3227	1775	Violle.
Iridium	3542	1950	"

The higher points in this table, especially those with respect to iron, are subject to considerable uncertainty.

90. Change of density produced in the act of melting. It is probable that most substances expand in the process of melting, so that the liquid is of smaller specific gravity than the solid; but there are some which contract. Ice is

a familiar instance of this latter class, being considerably lighter, bulk for bulk, than water. According to M. Brunner (fil.), (Art. 40), the density of ice at 0°C is only 0.91800, that of water at 4°C being reckoned equal to unity. The force with which water expands when it becomes ice is very great. On the other hand, mercury, phosphorus, paraffin, spermaceti, and many other substances, contract as they become solid.

91. Latent heat of fusion. When heat is applied to a pound of ice at the temperature of 0°C , the ice is not instantly converted into water, but the process is very gradual. The reason of this is that a large amount of heat must first enter into the pound of ice at 0° before it becomes water at 0° . This heat is called latent, because it is absorbed by the ice without producing any rise of temperature; and we may roughly represent to ourselves the process of liquefaction by the following formula:—

Water at 0° = ice at 0° + latent heat.

All substances in passing from the solid to the liquid state absorb heat, and we shall afterwards show how the amount of this may be measured. That absorbed by water is very great. The doctrine of latent heat was first taught by Dr. Black of Edinburgh. The great latent heat of water serves to retard the melting of snows. If snow or ice at 0° were suddenly to be converted into water by the smallest addition of heat the inhabitants of valleys would be exposed to terrific inundations, whereas by the gradual melting of ice this is prevented, and by the same means also these inhabitants are furnished with a continuous supply of water.

92. Influence of pressure upon the melting point. Professor James Thomson of Belfast anticipated theoretically the truth that the melting point of a body which expands in congelation would be lowered by increase of

pressure, while that of a body which contracts in congelation would be raised by it. We shall afterwards (Art. 401) give the reasoning by which this conclusion was arrived at; in the meantime we will content ourselves with stating that his brother's idea was verified experimentally by Lord Kelvin (Professor Sir W. Thomson of Glasgow), who showed that by a pressure of 16.8 atmospheres the freezing point of water (a substance which expands when freezing) was reduced 0.232° Fahr. (0.13° C).

These conclusions are in accordance with certain experiments originally made at Quebec by Major Williams and repeated by Boussingault, which showed that when the resistance of the envelope surrounding freezing water exceeds the expansive force developed, that resistance prevents the formation of ice, so that the water will remain fluid.

Bunsen afterwards found that the melting points of paraffin and spermaceti, both of which contract when freezing, were raised by the application of pressure. Thus spermaceti solidified at 47.72° C under the atmospheric pressure, but under a pressure of 156 atmospheres it solidified at 50.89° C.

Hopkins made similar experiments, not only on spermaceti, but also on wax and stearin; and finally, Mousson, by the enormous pressure of 13000 atmospheres, was able to lower the temperature of freezing water from 0° to -18° C.

93. Alloys and Fluxes. The fusing point of a mixture of bodies is often considerably lower than that of either of its components: thus, for instance, an alloy of five parts of tin and one of lead fuses at 194° C. In like manner Rose's fusible metal, consisting of four parts of bismuth, one of lead, and one of tin, fuses at 94° C, a temperature lower than that of boiling water. Alloys are much used in soldering and in taking casts.

Similar results are produced by mixing salts together: thus a mixture of the chlorides of potassium and of sodium melts at a lower temperature than either of its constituents. A mixture of equivalent quantities of carbonate of sodium and carbonate of potassium melts below the fusing point of either salt separately, and is used to facilitate the fusion of certain minerals in analysis. In like manner, fluxes are substances which, when added to an ore, promote the formation of a fusible medium.

94. Solution. Substances which change their composition in passing from the solid to the liquid state. If we have a standard solution of any salt at the bottom of which are crystals of the same salt, as long as the temperature remains the same there will be no change in the aspect of these crystals; but in most cases a rise of temperature will cause some of them to dissolve and assume the liquid state.

95. Freezing mixtures. In solution, just as in fusion, a certain quantity of heat becomes latent; and this is sometimes taken advantage of to produce intense cold. If two solids, or at least one liquid and one solid, on being mixed together produce a compound which is not solid but liquid, we have generally the production of cold.

The theory of freezing mixtures has been studied by Professor Frederick Guthrie (*Proc. Phys. Soc.*, 1875). He took in the first place some weak brine (one part of chloride of sodium and 24.2 parts of water) and found on subjecting it to cold that *pure ice* began to be formed at $-1^{\circ}.5\text{C}$. The formation of pure ice continued, and the temperature sank until -22°C was reached, the brine of course always becoming richer and richer in salt.

He next took saturated brine and found that the application of cold caused it to become poorer and poorer; thus for instance:—

		Per cent.
Saturated brine	at 0° contained	26.2724 of NaCl
Mother liquor after keeping at	-10° "	24.6528 "
" "	-16° "	24.1182 "
" "	-21° to -22° "	23.8874 "

It is thus clear that down to -22° the solidification impoverishes the brine, a result which Professor Guthrie remarks is inconsistent with the formation of ice alone as in the case of weak brine. He next took a quantity of brine which had been impoverished by being kept for an hour at -21° to -22° and subjected it to very intense cold, when the whole solidified and the temperature remained constant at -22° to -23° until the last drop had frozen; it then sunk rapidly.

The next remark is, that a salt-ice freezing-mixture is just capable of impoverishing saturated brine by withdrawal of salt-rich ingredients to such an extent that the unsolidified part is homogeneous in the sense of being solidifiable as a whole. Therefore -22° is the lowest temperature to be got by a salt-ice freezing-mixture.

Also the liquid portion of a salt-ice freezing-mixture is a brine of such a composition as to resist solidification at the temperature of the freezing-mixture. And hence the liquid portion of a freezing-mixture has the same composition as the mother-liquor of a saturated brine from which the salt-rich ingredients have been separated by the external application of a freezing-mixture.

These conclusions, which extend to other substances besides NaCl, are next shown to be favourable to the precision of the temperatures given by freezing-mixtures, and accordingly Professor Guthrie finds that such temperatures are very constant and comparatively independent both of the temperature of the salt employed and of the exact proportion used, and he appends the following table in which low temperature is obtained by mixing the salt

which we read the column of mercury, even if correct, only denotes true inches and parts of an inch at 62°Fahr., if it be of English construction, so that at any other temperature allowance must be made not only for the change in density of the mercury but for the change in length of the divisions of the scale.

Example.—Suppose that an English barometer with a brass scale, correctly graduated, reads 30 inches at 45°Fahr., what is the pressure in true inches of mercury reduced to its specific gravity at 32°Fahr.?

Since the scale is only correct (Art. 70) at 62°Fahr., and since brass expands very nearly .00001 for 1°Fahr., it follows that 30 apparent inches at 45°Fahr. = $\frac{30}{1.00017} = 29.995$ true inches. Also the density of mercury at 32°Fahr. (or 0°C) is to its density at 45°Fahr. (or 7°.2 C) as 1.001294 to 1. Hence the atmospheric pressure in mercury at 32°Fahr. will be $\frac{29.995}{1.001294} = 29.956$ inches.

In French barometers, on the other hand, the indications of the scale are correct at 0°C, the same temperature to which the mercurial column is reduced, while the scale itself represents millimètres.

In comparing an English and a French barometer it is therefore necessary to reduce the indications of each to 32°Fahr.; that is to say, to find by the one the pressure of the air in inches of mercury at 32°Fahr., and by the other the same in millimètres of mercury at 0°C. If both instruments are correct, their indications should then bear to one another the same ratio as a millimètre to an inch.

83. Expansion and contraction of metals. It requires the application of very intense pressure to produce the same change of volume in a solid or liquid body as that which is occasioned by a very small change of temperature.

It follows from this that the forces exerted by solids in contracting or expanding, and by liquids in expanding, must be very great. If a strong vessel be entirely filled with a liquid and then sealed tightly, the vessel will burst if there be a considerable rise of temperature.

In like manner it has been calculated, that a bar of wrought iron whose temperature is 15° Fahr. above that of the surrounding medium, if tightly secured at its extremities, will draw these together with a force of one ton weight for each square inch of section on cooling down to the surrounding temperature.

This property was first made use of in Italy to pull together walls which had bulged outwards. Iron bars were placed across the building and secured when in a heated state to the walls. As the iron cooled it contracted and the walls were thereby pulled together.

The same device was afterwards practised in Paris, and also in Ireland when repairing the cathedral at Armagh.

As another instance of the advantage which may be derived from the force of contraction, we may mention the familiar method by which tires are secured on wheels;—the tire is put on hot, when it fits loosely, but on its contraction in cooling it grasps the wheel with great force.

In all the arts it is of great importance to bear in mind the intensity of this force, sometimes with the view of guarding against its action, and sometimes in order to make it useful. Thus bars of furnaces must not be fitted tightly at their extremities, but must at least be free at one end. In making railways also a small space must be left between the successive rails.

Allowance must also be made for expansion and contraction in the case of tubular and lattice bridges. The reader who has visited the Menai tubular bridge will have observed the telescopic arrangement made for this purpose.

For a similar reason water or gas pipes are fitted to each other by telescopic joints; and, generally speaking, the effects which may follow change of temperature must always be taken into account by the constructor or engineer.

It is probably owing to the sudden change of volume from rapid cooling that tempered steel acquires that hardness which renders it so invaluable in the arts.

CHAPTER VI.

Change of State.—Liquefaction and Solidification.

84. Very many of the substances with which we are acquainted may be made to appear before us either in the solid, the liquid, or the gaseous condition; but there are others that can only be compelled to do so with very great difficulty.

Heat is the well-known agent which causes change of state; and it always acts in such a manner that a substance passes from the solid to the liquid, and from the liquid to the gaseous state, by the addition of heat, and back again in the reverse direction by the withdrawal of this agent. This law is quite universal, and the order is never reversed; so that, although we cannot as yet solidify alcohol, we are quite sure that our only chance of success lies in abstracting heat from this liquid; and in like manner, although we have not as yet succeeded in melting some substances, we are sure that if we ever succeed it will be by the application of great heat.

85. Let us in the first place study the passage of bodies from the solid to the liquid state.

The characteristics of these states are too well known to need lengthened description. We are all acquainted with the rigidity and permanence of form of a solid, and with the excessive mobility of a liquid which enables it readily to assume the form of the vessel in which it is placed; nevertheless, although nothing is more marked than the difference between the characteristic properties of solidity and liquidity, there is a set of bodies that possess properties intermediate to those of these two states, and receive the name of viscous bodies. Treacle is a body of this kind.

86. If a substance be capable of assuming the viscous state, we find that it does so before it begins to melt, and that it passes gradually from a solid state through a semi-solid viscous state to that of a liquid of evident mobility. Sealing-wax is a very good example of a substance of this nature; when cold it is brittle, when heated it first of all grows plastic and finally melts. In like manner, before fluidity iron loses its hardness and becomes soft to such an extent that pieces may be easily welded together or moulded into any form; and this property of iron greatly enhances its value in the arts. Other substances might be mentioned, and a gradual passage from the solid to the liquid state characterizes a large number of bodies. Furthermore, certain substances even after they have become unmistakably solid acquire certain properties, such as hardness and brittleness, in greater degree as the temperature continues to fall. Indeed, most of our hard bodies have high melting points, and the diamond, which is the hardest, is not susceptible of fusion at even the highest temperature hitherto obtained.

With many substances, however, the change from the solid to the liquid state is very abrupt, and such substances afford the means of indicating with very great precision, by their altered appearance, the attainment of certain

temperatures. Thus the temperature at which ice begins to melt is, under ordinary circumstances, a constant point, and is so used in the construction of thermometers.

87. But while there is a marked difference between bodies as to the abruptness with which they change their state, there is also a class of substances which change their composition in the act of changing their state. Such are saline solutions. In many of these a greater quantity of salt is retained in solution at a high temperature than at a low one, so that, when they are left to cool, crystals of salt are deposited.

With weak saline solutions, such as sea water, we have however a phenomenon of a somewhat different nature when the temperature is lowered. At a certain point which is constant for a solution of the same strength, the water solidifies as nearly pure ice, leaving the salt behind.

In what follows we shall distinguish between those substances which do not, and those which do, change their composition in changing their state. Also, our remarks must be taken as referring to substances in which the passage from the one state to the other is not gradual but abrupt.

PASSAGE FROM THE SOLID TO THE LIQUID STATE,
OR LIQUEFACTION.

88. **Fusion.** Substances which do not change their composition in passing from the solid to the liquid state. The following laws are observed by all such when melting.

1. *Each substance begins to melt at a certain temperature, which is constant for the same substance if the pressure be constant.*
2. *The temperature of the solid remains at this constant*

point from the time when fusion commences until it is complete.

3. If a substance expands in congelation its melting point is lowered by increase of pressure, but if a substance contracts in congelation its melting point is raised by increase of pressure.

89. The following table contains the melting points of various substances under the ordinary atmospheric pressure.

Table of melting points.

Name of substance	Temp. of melting point		Observer
	Fahr.	Cent.	
Mercury	-37.9	-38.8	Stewart.
Oil of vitriol	-30	-34.4	Regnault.
Bromine	+ 9.5	-12.5	Pierre.
Ice	32	0.0	
Phosphorus	111.5	44.2	Schrötter.
Potassium	136	57.8	Regnault.
Sodium	207.7	97.9	"
Sulphur	239	115.0	Person.
Tin	451	232.8	"
Bismuth	512	266.7	"
Lead	620	326.7	"
Zinc	680	360	Pouillet.
Antimony	810	432	"
Aluminium	1157	625	Le Chatelier.
Silver (pure)	1749	954	Violle.
Gold (pure)	1895	1035	"
Copper	1929	1054	"
Palladium	2732	1500	"
French wrought iron	2732	1500	Pouillet.
English wrought iron	2912	1600	"
Platinum	3227	1775	Violle.
Iridium	3542	1950	"

The higher points in this table, especially those with respect to iron, are subject to considerable uncertainty.

90. **Change of density produced in the act of melting.**
It is probable that most substances expand in the process of melting, so that the liquid is of smaller specific gravity than the solid; but there are some which contract. Ice is

a familiar instance of this latter class, being considerably lighter, bulk for bulk, than water. According to M. Brunner (filis), (Art. 40), the density of ice at 0°C is only 0.91800, that of water at 4°C being reckoned equal to unity. The force with which water expands when it becomes ice is very great. On the other hand, mercury, phosphorus, paraffin, spermaceti, and many other substances, contract as they become solid.

91. Latent heat of fusion. When heat is applied to a pound of ice at the temperature of 0°C , the ice is not instantly converted into water, but the process is very gradual. The reason of this is that a large amount of heat must first enter into the pound of ice at 0° before it becomes water at 0° . This heat is called latent, because it is absorbed by the ice without producing any rise of temperature; and we may roughly represent to ourselves the process of liquefaction by the following formula:—

Water at 0° = ice at 0° + latent heat.

All substances in passing from the solid to the liquid state absorb heat, and we shall afterwards show how the amount of this may be measured. That absorbed by water is very great. The doctrine of latent heat was first taught by Dr. Black of Edinburgh. The great latent heat of water serves to retard the melting of snows. If snow or ice at 0° were suddenly to be converted into water by the smallest addition of heat the inhabitants of valleys would be exposed to terrific inundations, whereas by the gradual melting of ice this is prevented, and by the same means also these inhabitants are furnished with a continuous supply of water.

92. Influence of pressure upon the melting point. Professor James Thomson of Belfast anticipated theoretically the truth that the melting point of a body which expands in congelation would be lowered by increase of

pressure, while that of a body which contracts in congelation would be raised by it. We shall afterwards (Art. 401) give the reasoning by which this conclusion was arrived at; in the meantime we will content ourselves with stating that his brother's idea was verified experimentally by Lord Kelvin (Professor Sir W. Thomson of Glasgow), who showed that by a pressure of 16.8 atmospheres the freezing point of water (a substance which expands when freezing) was reduced 0.232° Fahr. (0.13° C).

These conclusions are in accordance with certain experiments originally made at Quebec by Major Williams and repeated by Boussingault, which showed that when the resistance of the envelope surrounding freezing water exceeds the expansive force developed, that resistance prevents the formation of ice, so that the water will remain fluid.

Bunsen afterwards found that the melting points of paraffin and spermaceti, both of which contract when freezing, were raised by the application of pressure. Thus spermaceti solidified at 47.72° C under the atmospheric pressure, but under a pressure of 156 atmospheres it solidified at 50.89° C.

Hopkins made similar experiments, not only on spermaceti, but also on wax and stearin; and finally, Mousson, by the enormous pressure of 13000 atmospheres, was able to lower the temperature of freezing water from 0° to -18° C.

93. Alloys and Fluxes. The fusing point of a mixture of bodies is often considerably lower than that of either of its components: thus, for instance, an alloy of five parts of tin and one of lead fuses at 194° C. In like manner Rose's fusible metal, consisting of four parts of bismuth, one of lead, and one of tin, fuses at 94° C, a temperature lower than that of boiling water. Alloys are much used in soldering and in taking casts.

Mr. Charles Tomlinson made in 1868 a series of very interesting experiments on supersaturated saline solutions, and he came to the conclusion that those substances which induce crystallization do so in consequence of not being chemically clean. The subject has likewise been investigated by Professor Liversidge and Mr. John M. Thomson. This last experimenter believes, as the results of his experiments, that truly isomorphous bodies—that is substances possessing the same chemical composition and crystalline form—are active in causing the sudden crystallization of each other.

108. If instead of a saturated solution we have a weak solution of certain salts, such as sea water, this, when lowered in temperature, will change its state in a different way. At a temperature which is always lower than the freezing point of water such a solution will freeze, producing a nearly pure ice and leaving the salt behind. We have already (Art. 95) recorded the experiments made by Professor Guthrie on this subject.

CHAPTER VII.

Change of State.—Production of Vapour and its Condensation.

109. When sufficient heat is applied to a body it generally assumes the gaseous state; unless it be of such a nature that it will under ordinary circumstances be decomposed before assuming this state. By means of a certain application of electricity it is probable that the most refractory substances, such as carbon, can be made to appear as gases, although only in very small quantity.

Generally when a solid passes into the gaseous state it

first assumes the intermediate state of a liquid, but sometimes its passage into the gaseous state is completed without the intermediate form of liquidity being assumed. This is called *sublimation*; while the passage of a liquid to the gaseous state goes under the general name of *vaporization*. In whatever way the gaseous condition is produced it always requires a considerable amount of latent heat. Thus a pound of water at 100°C will absorb a great quantity of heat before it is entirely converted into steam, although the steam does not possess a higher temperature than 100° . In the same manner as before we may apply the following formula, and roughly say:—

Steam at 100° = water at 100° + latent heat of steam.

The latent heat of gases is greater than that of liquids, and we shall afterwards show how it may be measured. This latent heat has to be disposed of in some sensible form, when the gas which possesses it is reconverted into a liquid, and thus the latent heat of gases is of great service in retarding the change from the liquid to the gaseous or from the gaseous to the liquid state, which, but for the great latent heat of gases, would be inconveniently sudden.

Elastic fluids have been divided into gases and vapours, but the distinction between these is merely conventional. A vapour denotes a substance in the gaseous form which at ordinary temperatures appears as a liquid or solid, while a gas denotes a substance which under ordinary circumstances appears in the gaseous form, and which can only be reduced to the solid or liquid form by intense pressure or intense cold. It has, however, been proposed to distinguish between these terms, vapour and gas, by applying them to a substance in the gaseous form according as its temperature is respectively lower or higher than a certain—the critical—temperature (see Art. 131).

Our subject may be divided into the following parts :—

1. Vaporization, or the conversion of a liquid into a gas ; and sublimation, or the conversion of a solid into a gas.
2. Liquefaction and solidification of vapours and gases.
3. Pressure and density of vapours and gases, with a few remarks upon hygrometry.

VAPORIZATION AND SUBLIMATION.

110. Vaporization is the general name for a process of which there are three varieties, namely :—

1. *Evaporation*, where a liquid is converted into a gas quietly, and without the formation of bubbles.
2. *Ebullition*, where bubbles of gas are formed in the mass of the liquid itself.
3. Vaporization in the *spheroidal condition*, where a liquid evaporates slowly, although in apparent contact with a very hot substance.

111. Vapours are formed in vacuo more readily than in air. The presence of air or of any foreign gas retards the formation of vapours, but in vacuo a liquid is very quickly converted into vapour. If a small quantity of water, alcohol, or ether be introduced up through a barometer tube into the Torricellian vacuum at the top, as soon as it reaches this it is converted into vapour, which shows itself by lowering the column of mercury by means of the pressure which it exerts. This column, which originally denoted the pressure of the atmosphere, now denotes the pressure of the atmosphere *minus* the pressure of the vapour of the liquid.

112. *Maximum of pressure in vacuo.* If we continue to introduce an additional quantity of the volatile fluid into the Torricellian vacuum of a barometer, we shall at first probably perceive an additional depression ; but as we go on we shall find that the depression does not increase

beyond a certain limit, or, in other words, the pressure of the vapour we have introduced has reached a maximum, and the introduction of more liquid will not increase the density of the vapour. We shall further find that the maximum of pressure is regulated by the temperature in such a manner that the higher the temperature the higher is the maximum pressure, so that we are enabled to deduce the following law, first discovered by Dalton :—*In space destitute of air the vaporization of a liquid goes on only until the vapour has attained a determinate pressure dependent on the temperature, so that in every space void of air which is saturated with vapour determinate vapour pressure corresponds to determinate temperature.*

Mr. John Aitken has recently made some experiments which tend to show that small particles have an action in promoting the condensation of aqueous vapour somewhat similar to that which they have in promoting crystallization from a supersaturated solution. The dust of the air may thus possibly be a factor of some importance in meteorology.

113. Mixtures of gas and vapour in a confined space.
The experiments of Dalton lead to the following law :—*In a space filled with air the same amount of water evaporates as in a space destitute of air ; and precisely the same relation subsists between the temperature and the pressure of the vapour, whether the space contains air or not.*

Thus if a closed space contain dry air of the pressure of 30 inches at a temperature for which the pressure of aqueous vapour is 2 inches, and if a little water be introduced, the pressure will rise to 32 inches ; while if the same space be void of air the pressure of the aqueous vapour will of course be 2 inches. This law of Dalton has been verified by Gay-Lussac. More lately, Regnault has made experiments on this subject, and has investigated the

pressures of the vapours of water, ether, bisulphide of carbon, and benzole, both in *vacuo* and in air. He has found that the pressure in air is always slightly less than it is in *vacuo*, the difference being greater for volatile liquids; but he is inclined to believe that Dalton's law is true in principle, and that the differences which he observed were caused by the hygroscopic properties of the sides of the chamber which contained the vapours.

114. Mixed liquids in a confined space. Where a mixture of liquids is allowed to evaporate in a closed space, Gay-Lussac inferred that the pressure of the mixed vapour was equal to the sum of the pressures of the two vapours taken separately.

Magnus and Regnault have found that this holds for a mixture of bisulphide of carbon and water, or of benzole and water, of which the components do not dissolve each other; but in other cases it does not hold.

Thus for a mixture of ether and water the pressure is scarcely higher than for ether alone. If the liquids mix readily together in all proportions, then the vapour pressure is generally less than that of the one liquid and greater than that of the other.

115. Effect of chemical affinity upon evaporation. If water be put into a confined space along with some substance which has a great attraction for it and does not readily part with it, the vapour density may be much diminished. Thus if a small quantity of water be mixed with a large quantity of sulphuric acid, the acid will retain the water and will not suffer any of it to evaporate.

On the other hand, if we have a large quantity of water and an exceedingly small quantity of acid, we shall have very nearly the usual pressure of vapour.

Between these two extremes we may prepare solutions of intermediate strength which will diminish to a greater or

less extent the pressure of aqueous vapour corresponding to the temperature of observation.

A similar rule will hold for other solutions; and if the substance mixed with the liquid whose pressure in a state of gas is sought be a fixed and not a volatile body, its tendency will generally be to prevent the liquid from evaporating, and thus to diminish the pressure due to vapour.

116. Pressure when two vessels at different tempera-

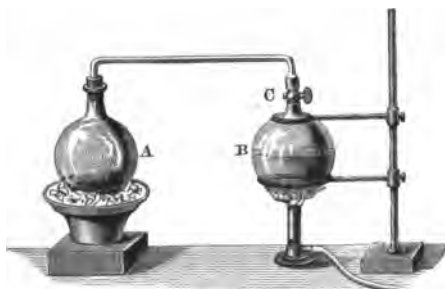


Fig. 24.

tures are in communication with each other. In Figure 24, let us first suppose that the stop-cock at *C* is shut, and that two similar vessels *A* and *B* are entirely filled with water and vapour of water to the exclusion of air or any other gas. Also let *A* be surrounded with ice, and let heat be applied to *B*, so that we may suppose *A* to be at the temperature of melting ice and *B* to be at 100°C . In this case the pressure of the vapour in *A* will hardly be one-fifth of an inch, while in *B* it will be nearly 30 inches. Now on opening the stop-cock, there will of course be a rush of vapour from *B* to *A*, and we may suppose that for a moment the pressure of the vapour will be the mean between the two original pressures, but the effect of the cold surface of *A* will be to condense this vapour and to

render it as nearly as possible equal to the pressure at 0° , viz. one-fifth of an inch. If there be water in *B* more vapour will rise and pass to *A*, there to be condensed as before. In fact, the apparatus will now act as a still, and the water of *B* will be gradually transferred to *A*. The latent heat, set free by the large quantity of vapour which is condensed at *A*, will of course tend to raise the temperature of *A*; but provided that this temperature be kept steadily at or near 0° by a sufficiently powerful application of cold, the pressure in *A* will by this arrangement be kept very low, while the pressure of vapour in *B* will be somewhat higher than in *A*, and the dynamical effect of this inequality of pressure in these two vessels will be represented by the rush of vapour from *B* to *A*. The intensity of this rush will depend on the intensity of the source of heat: if the heat which enters *B* be sufficient to produce a large quantity of vapour in a short time, this vapour will rush very fast towards *A*, and a powerful freezing mixture will have to be applied in order to keep down the temperature of *A*, but if the source of heat be feeble the rush will be feeble also; in fact, by this arrangement the vapour of water may be regarded as a vehicle for transferring the heat from the source at *B* to be spent in liquefying the ice or freezing mixture, or to be otherwise disposed of at *A*.

If in the first part of this experiment, when the cock *C* is shut, the vessel *B* contains no water in a liquid form, but is entirely filled with the vapour of water at 100° , then when *C* is opened this vapour will be almost immediately condensed at *A*, and an approximate vacuum will be formed. We shall afterwards see how this principle has been applied by Watt in the steam-engine (Art. 355).

It will be evident that the perfection of vapour as a vehicle for carrying heat, as described above, depends

upon the absence of air in the arrangement of the experiment.

For if *A* and *B* be filled with air, each particle of vapour which is carried from *B* to *A* must pass through all this air, and the transmission of vapour will in this case be very difficult. Professor O. Reynolds (Proc. R. S., 1873) shows that a small quantity of air in steam does very much to retard its condensation upon a cold surface.

The following are various useful applications of the process described above.

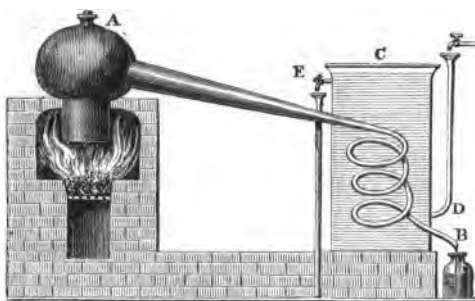


Fig. 25.

117. Distillation. The subjoined figure will represent this process. The liquid to be distilled away is contained in *A*. It generally exists combined either with some fixed impurities or with some other liquid less volatile than itself, and the object of distillation is to separate it from these. This is done by applying heat to *A* and by attaching to it a tube, as in Fig. 25, the other extremity of which passes in coils through a vessel of cold water. The liquid is vaporized by the applied heat, and is then driven through this tube, but as it passes through the coils immersed in the cold water (technically called *the worm*), a comparatively large surface is exposed to the cooling agent, and the

vapour is rapidly condensed, passing in drops from *B* into a bottle prepared to receive it. The vessel *C* through which the worm of the still passes must be kept cold; this is done by constantly supplying it at a low level with cold water by means of a tube at *D*, and by withdrawing the hotter and therefore lighter layers of the water at *C*; a constant current of cold water is thus made to circulate through the vessel.

118. Cold due to evaporation. Freezing apparatus. Whenever vapour is produced a quantity of heat is rendered latent. This heat is necessary to the formation of vapour, and must be supplied either from some foreign source, or, if this be not available, from the very liquid which is being evaporated. In this last case the temperature of the liquid falls in order to supply the heat necessary to the existence of vapour.

Leslie was the first to freeze water by means of the drain of heat caused by its own evaporation.

In his experiment a vessel, Fig. 26, containing strong sulphuric acid is placed under the receiver of an air-pump, and above it a thin metallic vessel containing a little water. As the receiver becomes exhausted the water evaporates more and more rapidly, and the vapour, as fast as it is formed, is absorbed by the sulphuric acid. The vapour thus becomes a vehicle for carrying heat from the metallic vessel, and the consequence is a diminution in temperature



Fig. 26.

until ice is formed. Air-pumps are now constructed by means of which water may be frozen almost in the very act of boiling. They contain reservoirs of sulphuric acid into which the vapour drawn from the water is forced at each stroke of the pump.

An instrument called the cryophorus, or frost carrier (*κρύος frost, φερός bearing*), very similar to that of Fig 24, is sometimes used to show the freezing of water from its own evaporation. Thus if we suppose all the water to be in *B*, and only vapour of water without air in *A*, and if *A* is cooled by a powerful freezing mixture, while *B* is not exposed to a source of heat, then rapid evaporation of the water in *B* will take place, and this vapour will go to *A* and be condensed there as fast as it is formed.

Heat is thus carried, as before, from *B* to *A*, but as there is now no source of heat at *B* the water there must part with its own heat in order to furnish that which is necessary for evaporation, in consequence of which it will be frozen. In this experiment it is well to protect *B* from the influence of currents of air.

When other liquids and mixtures more volatile than water are used in this manner, a very intense cold may be produced. Thus by the evaporation of liquid sulphurous acid a degree of cold is obtained sufficiently strong to freeze mercury.

By a mixture of solid carbonic acid and ether Thilorier obtained a temperature of about -77°C , and Faraday, by placing this mixture in a vacuum, produced a degree of cold which he estimated at -110°C ; a little later, Natterer, by mixing liquid nitrous oxide with bisulphide of carbon, and placing them both in vacuo, obtained -140°C ; and recently, by the evaporation of liquid oxygen under a pressure of 14 millimètres of mercury, Dewar and Fleming have obtained a temperature of $-223^{\circ}\cdot 2\text{C}$ as indicated by a platinum thermometer (Art. 31a).

In hot climates porous vessels called alcarazas are used for cooling water. The water reaches the outside through the pores, and hence a continual evaporation is going on, especially when the vessels are placed in a current of air.

MM. Carré and Co. of Paris have invented a very ingenious freezing machine, which was exhibited in London at the International Exhibition of 1862.



Fig. 27.

Before using the instrument it is laid upon its side, boiler downwards, for about 10 minutes, so as to allow

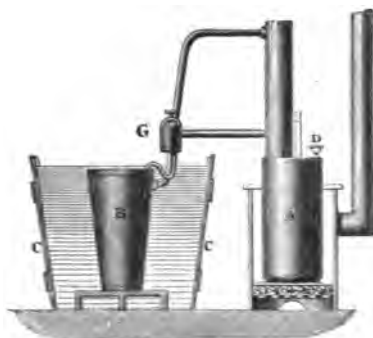


Fig. 28.

any liquid that may be in the condenser to drain back into the boiler, and this is facilitated by heating the condenser slightly with a lamp. The process consists of two parts. In the first of these, Fig. 28, the boiler is heated very gradually by a charcoal chauffer, or other source of heat,

This apparatus is represented in Figs. 27 and 28. *A* is a strong vessel of wrought iron three-quarters filled with a concentrated solution of ammonia. *B* is a strong wrought iron circular condenser having a central space sufficiently large to receive the vessel *D*. The pipes are so arranged as to prevent the liquid from boiling over into the condenser.

Before using the instrument it is laid upon its side, boiler downwards, for about 10 minutes, so as to allow any liquid that may be in the condenser to drain back into the boiler, and this is facilitated by heating the condenser slightly with a lamp. The process consists of two parts. In the first of these, Fig. 28, the boiler is heated very gradually by a charcoal chauffer, or other source of heat,

of this process, the ammoniacal gas separates from the water and is condensed by its own pressure in *B*, and the heating is allowed to go on until a thermometer attached to the boiler indicates about 132°C , at which temperature it is presumed that nearly all the ammoniacal gas is condensed in *B*, while all the water remains behind in *A*: the second part of the process next begins.

The apparatus is now withdrawn from the fire; the water is allowed to run out of the orifice *B* through a hole in the bottom; the orifice is then stopped with a cork, and the cylinder *D* containing the liquid to be frozen is put into *B*, a little alcohol having been previously introduced in order to establish a liquid communication between the sides of *B* and *D*; the vessel *A* (Fig. 27) is now plunged into water which is kept cool, while the condenser is wrapped round with flannel, which is well known to be a non-conductor. The temperature of *A* now falls very rapidly, and as the water in *A* *reacquires* its power of absorbing ammoniacal gas, this gas rises very abundantly from *B*, and is condensed in *A*.

In consequence of this rapid evaporation *B* becomes intensely cold, and if it contains water this will be frozen. Mercury may also be frozen by this means.

As the success of this instrument depends upon its being devoid of air, there is an arrangement of the following kind, by which any air can be got rid of. *G* is a small cup which is always kept full of water, and in it works a screw, so that when relaxed it opens up an exceedingly small entrance into the interior. When the temperature of the boiler has risen to about 60°C the screw is slightly loosened, and the disengaged ammoniacal gas is rapidly absorbed by the water in *G*. If any air be present, this will be seen by its rising to the surface, and the channel must be kept open so long as such an appearance of air continues, but when

the gas is wholly dissolved by the water, the screw must be again tightened and the operation of heating continued.

A portion of the boiler at *D*, Fig. 28, is made of metal which will fuse below that temperature at which the pressure of the steam would burst the boiler. This arrangement acts therefore as a safety-valve.

In 1877-8 M. Cailletet of Paris and M. Raoul Pictet of Geneva succeeded in obtaining in the solid or liquid state the gases hitherto uncondensed. Their plan was to subject the gas at once to great pressure and great cold, and then by suddenly relieving the pressure the expansion produced so diminished the temperature as to condense the gas.

119. Pressure in communicating vessels filled with air. Dalton, as we have already mentioned, was the first to show that in a space filled with air the same amount of water evaporates as in a space destitute of air; and that precisely the same relation subsists between the temperature and the maximum vapour pressure whether the space contains air or not. Unfortunately there has been based upon this experimental result a theory which is *only a possible but not a necessary* result of these experiments. It has been supposed that no mutual relation whatever exists between vapour and air, and that they remain near each other producing the slightest mechanical effect upon one another. This theory has come to be too much regarded as a necessary result of Dalton's experiments, although certain observations made by Bessel, Broun, Welsh, and others seemed to be incapable of explanation by it. Dr. Lamont of Munich has devised a crucial experiment, the result of which has been to refute this hypothesis. The arrangement adopted was of the following nature. A glass tube, bent as in Fig. 29, has at one end a globe *K*, while the other end *e* is left open to the atmosphere; *q* is a drop of quicksilver, which is capable of moving backwards

and forwards along *de*. The curved part *ckd* of the tube is plunged into a vessel *BB* filled with cold water, while into the vessel *AA*, in which the globe *K* is placed, cold and warm water can alternately be poured. The experiment was of the following nature: suppose that before commencing it the temperature of the whole apparatus as well as of the water in *BB* is 0°C , and suppose also that the globe and tube are filled with dry air of the pressure of 30 inches.

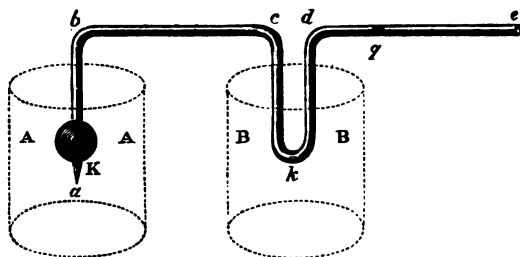


Fig. 29.

First raise the temperature of the globe *K* to 40°C by pouring warm water into *AA*, while the temperature of *bcd* remains as before. Owing to the increased volume of the dry air, the quicksilver *q* is pushed toward *e*;—notice how far.

Next cool down the globe to its former temperature (0°), and introduce a little water *K* by breaking off the fine point *a*, which is then sealed on again, and repeat the previous experiments—that is to say, heat the globe to 40°C , as before, and again notice how far the quicksilver is pushed towards *e*.

The result of this experiment will be a test of the truth of this hypothesis. Let us see, in the first place, what ought to take place if these views are correct; that is to

$$1000 \text{ BTU} = \int_{\pi}^{212}$$

say, if the vapour and air are quite independent of each other. For simplicity's sake we may imagine the second heating of the globe to take place not a very long time after the introduction of the water, in which case the vapour will not yet have penetrated to q (in Lamont's experiment there was no trace of vapour at this part of the apparatus). If these views be correct, there being no pressure of vapour at q , the pressure there will be entirely due to dry air. No doubt there is pressure of vapour in the globe K , but by this hypothesis it has no effect on the particles of dry air, and cannot therefore be communicated to q . The drop of quicksilver at q ought therefore to move, for a given heating of the ball, precisely the same distance whether the air of the globe be dry or whether it contain vapour.

Let us now suppose, instead of this hypothesis, that the air exerts a pressure upon the vapour and the vapour upon the air. Then the globe K will have a pressure of vapour corresponding to 40°C (104°Fahr.), which by Table I at the end of the volume is 2.16 inches; this has to be added to the pressure of dry air, and the sum will be communicated through the dry air of the tube to the quicksilver at q , which will, on this hypothesis, be pushed much farther when there is vapour than when there is only dry air. On the other hypothesis, however, as we have seen, the quicksilver will be pushed equally far in both cases. Now Lamont found that the quicksilver was pushed much farther when there were air and vapour together than when there was only dry air, and he therefore concluded that the first hypothesis is incorrect.

120. Various modes of vaporization. Our attention has hitherto been directed to certain laws which have no special reference to the particular modes in which vaporization is accomplished.

Let us now consider the peculiarities of these various modes. We have already (Art. 110) stated that there are three such—viz. *evaporation, ebullition, and vaporization in the spheroidal state.*

121. Evaporation. Evaporation denotes the quiet production of vapour at the surface of a liquid, and is subject to the following laws:—

1. It varies with the temperature.
2. It varies with the extent of surface exposed.
3. It goes on very rapidly in vacuo, but much more slowly in a space filled with air.
4. It goes on more rapidly in dry air than in air containing vapour.
5. It is assisted by any agitation tending to renew the particles of air over the evaporating surface.

The reason of the fourth and fifth laws is very evident. When vapour forms above the surface of a liquid in still air, it rises so slowly that the air above the liquid soon becomes saturated with vapour, or nearly so, and hence the evaporation, if not quite stopped, yet proceeds very slowly. But when new and comparatively dry particles of air are constantly brought into contact with the liquid the process is greatly facilitated.

This process is constantly going on in nature, and forms one of the means by which the surface of the earth is rendered fit for the maintenance of living beings; it is also of very extensive application in chemistry and in the arts, being employed to separate a volatile from a fixed substance.

122. Ebullition. When a liquid is heated in an open vessel it gradually becomes hotter, and the evaporation more and more rapid. After some time the layers of liquid in contact with the sides of the vessel become changed into vapour, which begins to rise, but is condensed by the

colder strata before it reaches the surface. This is the cause of the singing noise of liquids before they begin to boil. Soon, however, the bubbles of vapour are able to reach the surface, and the process of ebullition has begun. The temperature now ceases to rise, and remains stationary until the whole of the liquid has been boiled away.

The temperature of ebullition depends, (1) on the external pressure; (2) on the nature of the vessel; (3) on the substance dissolved in the liquid; (4) on the nature of the liquid.

123. Influence of pressure upon the boiling point.

It may be easily shown, by an arrangement like that of Figures 2 and 3, that the pressure of vapour during ebullition is equal to the external pressure, for it will be found that the level of the liquid is the same on both sides of the gauge.



Fig. 30.

We see now what takes place when a liquid is heated in the open air. Its temperature will continue to rise up to that point for which the corresponding vapour pressure is equal to the external atmospheric pressure. The temperature of the boiling point will thus be low when the pressure of the air is low, and high when this is high. The

following experiments will illustrate the effect of pressure.

Production and Condensation of Vapour. 123

First experiment.—Let a flask half filled with water, Fig. 30, be boiled until all the air has been driven out of the upper part of it, which is filled with steam instead. If it now be corked tightly and inverted, it will very soon cease boiling; but if cold water be poured upon it ebullition will commence anew: the reason being that the cold water by condensing the vapour with which the upper part of the flask is filled withdraws the pressure from the water, which is thus enabled to boil at a comparatively low temperature.

Second experiment.—Put a vessel containing ether under the receiver of an air-pump. Exhaust the receiver, and the ether will begin to boil at the ordinary temperature.

It follows from these experiments that at the top of a lofty mountain, where the pressure of the atmosphere is much diminished, the temperature of the boiling point of water will be much reduced. At the top of Mont Blanc, for example, water boils at about 85°C (185°Fahr.). The temperature of boiling water at high elevations is often too low for culinary purposes, and those who live in such places are therefore compelled to heat water in a closed vessel under a pressure greater than that of the atmosphere in order to prepare their food.

This is done by means of an apparatus invented by Papin, a French physician, which bears the name of Papin's Digester. It consists simply of a strong closed vessel containing the water



Fig. 31.

to which heat is applied. When the pressure rises too high the vapour escapes by means of a safety-valve. There is thus a limit depending on the strength of the vessel, beyond which the pressure and temperature cannot mount, but this limit is sufficiently high to permit of the contained water doing great service in culinary operations. This apparatus is also often used at ordinary levels, since water is much more efficient in extracting gelatine from bones at a high temperature than at the ordinary boiling point.

Boiling-point thermometers are sometimes used for indicating, by means of the temperature of ebullition, the pressure of the air, and thus determining the heights of mountains. Such instruments perform the part of a barometer, while they are more portable. Their scale embraces a temperature range generally extending only from about 20° below 100° to a few degrees above this point; it is thus very open, and the temperature of the boiling point may be very accurately observed. Mountain thermometers are accompanied by an apparatus similar to that of Fig. 2, devised by Regnault, and fitted in this case with telescopic joints, in order to make it easily portable.

124. Influence of the nature of the vessel upon the boiling point. Achard was the first to notice, in 1785, that the boiling point of water under a constant pressure is much more inconstant in metallic than in glass vessels. He also noticed that if, while water was boiling steadily in a glass vessel, a drachm of iron-filings or some other insoluble solid were added to the water, the boiling point was lowered 1° Réaumur or more, the depression varying according as the substance was in powder or in lump. On the other hand, the temperature of the vapour arising from the water is as nearly as possible the same in all these cases.

Hence we see that while the temperature of the vapour

remains constant, that of the liquid varies according to the nature of the vessel; we ought also to state that in all cases the temperature of the vapour of water is below that of boiling water.

125. Influence of substances dissolved upon the boiling point. Magnus, Marcet, and others have made experiments on saline solutions of different kinds and strengths, from which it appears that the general effect of the salt is to raise the temperature of ebullition. According to these experiments the salt has the effect of raising the temperature of the vapour as well as that of the liquid. Regnault, who has investigated this subject, concludes that the vapour is at first in temperature equilibrium with the boiling solution, but that it is quickly cooled, so that the results obtained by Rudberg, who found that the vapour of a solution possesses the same temperature as if it were disengaged from pure water at the same pressure, may be considered correct. In practice the temperature of the vapour of moderately pure water in an apparatus similar to that of Fig. 2 may be considered to be regulated entirely by the atmospheric pressure.

126. Influence of air dissolved upon the boiling point. Magnus had made the observation that if water could be boiled in a vessel formed as it were of water itself, or in a vessel the sides of which would retain the water everywhere with the same force as that which its particles exert upon each other, we should then know the true boiling point of water.

M. Donny was afterwards led to conclude that the boiling point of perfectly pure water is very high. By depriving the water of air as far as possible by long continued boiling and by enclosing it in a peculiarly shaped vessel, he was able to raise its temperature to 135°C without ebullition, and even higher temperatures have since been

obtained. M. Dufour found that globules of water suspended in an equally dense fluid remain liquid between -20°C and $+178^{\circ}\text{C}$. Sir W. R. Grove has also made experiments on this subject, and has found that even after water has been long boiled it is not quite deprived of all traces of nitrogen; and he has gone the length of saying that no one yet has seen the phaenomenon of *pure water* boiling, that is, of the disruption of the liquid particles of the oxy-hydrogen compound so as to produce vapour, which will condense into water, leaving behind no permanent gas.

Mr. C. Tomlinson (Proc. R. S., Jan. 21, 1869) has studied the subject of boiling liquids with much care. He starts by supposing that a liquid at or near the boiling point is a supersaturated solution of its own vapour constituted exactly like soda-water, Seltzer-water, and solutions of some soluble gases.

This being the case, he finds that ebullition is much facilitated in many cases by the action of nuclei or small foreign bodies, and that a solid non-porous nucleus is or is not efficient in liberating vapour, according as it is chemically unclean or clean. Porous bodies, however, are invariably active.

Mr. Tomlinson is inclined to think that too much importance has been attached to the presence of air and gases in water and other liquids as a necessary condition of their boiling.

127. Influence of the nature of the liquid upon the boiling point. Some liquids, such as ether and sulphurous acid, have very low boiling points, while others, such as mercury, have very high ones. The following table of boiling points and specific gravities has been constructed by the late Dr. W. A. Miller, and is derived chiefly from the labours of Pierre and Kopp.

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Table of boiling points and specific gravities of liquids.

Name of Substance.	Boiling point. Fahr. Cent.	Specific gravity at 0°C.	Observer.
Sulphurous anhydride . .	17.6 - 8.00	1.491	Pierre
Chloride of ethyle . . .	51.9 11.00	0.9214	"
Bromide of methyle . . .	55.5 13.05	1.6644	"
Aldehyde	69.4 20.78	0.8009	Kopp
Formiate of methyle . . .	92.1 33.39	0.9984	"
Ether	94.8 34.89	0.7365	"
Bromide of ethyle . . .	105.8 41.00	1.4733	Pierre
Iodide of methyle . . .	111.4 44.11	2.1992	"
Bisulphide of carbon . .	118.5 48.05	1.2931	"
Formic ether	127.7 53.17	0.9357	"
Acetone	133.3 56.28	0.8144	Kopp
Acetate of methyle . . .	133.3 56.28	0.9562	"
Chloride of silicon . . .	138.2 59.00	1.5237	Pierre
Bromine	145.4 63.00	3.1872	"
Wood-spirit	149.9 65.50	0.8179	Kopp
Iodide of ethyle	158.5 70.28	1.9755	Pierre
Acetic ether	164.9 73.83	0.9069	"
Alcohol	173.1 78.39	0.8151	"
Terchloride of phosphorus	173.4 78.55	1.6162	"
Benzole	176.8 80.44	0.8921	Kopp
Dutch liquid	184.7 84.83	1.2803	Pierre
Butyrate of methyle . . .	204.6 95.88	0.9209	Kopp
Water	212.0 100.00	1.0000	"
Formic acid	221.5 105.28	1.0267	"
Butyric ether	238.8 114.88	0.9041	"
Perchloride of tin . . .	240.0 115.66	2.2671	Pierre
Valerate of methyle . . .	241.1 116.17	0.9015	Kopp
Acetic acid	243.1 117.28	1.0619	"
Fusel oil	269.8 132.11	0.8271	Pierre
Bromide of ethylene . . .	270.9 132.72	2.1629	"
Terchloride of arsenic . .	273.0 133.88	2.2050	"
Perchloride of titanium .	276.6 135.88	1.7609	"
Bromide of silicon . . .	308.0 153.33	2.8128	"
Butyric acid	314.6 157.00	0.9886	Kopp
Sulphurous ether	320.0 160.00	1.1063	Pierre
Terbromide of phosphorus	347.5 175.28	2.9249	"
Sulphuric acid	640.0 337.77	1.8540	Marignac
Mercury	662.0 350.00	13.5960	Regnault

Kopp, as far back as 1841, pointed out that in analogous compounds the same difference of chemical composition

frequently involves the same difference of boiling points, and he has more particularly endeavoured to show that in a very extensive series of compounds (alcohols, acids, and compound ethers) the elementary difference CH^2 is attended by a difference of 19°C in the boiling point. Kopp has also made comparisons of the specific volumes ($\text{sp. vol.} = \frac{\text{atomic weight}}{\text{sp. gravity}}$) of different liquids, and finds that when these are compared at the respective boiling points of the liquids, or points of similar pressure, one arrives at very simple results.

128. Leidenfrost's Phaenomenon. Spheroidal state. Leidenfrost was the first who scientifically examined the curious phaenomenon which bears his name. He found that if a drop of water or other liquid be thrown upon a surface of high temperature, the liquid does not adhere to the surface but forms a spheroidal mass, which, if the heat be kept up, oscillates and moves about, evaporating meanwhile without boiling.

This phaenomenon, which has been named the caloric paradox, has in later years been the subject of much attention, and experiments have been contrived with the view of rendering its peculiarities as prominent as possible. Thus, for instance, M. Boutigny poured liquid sulphurous acid upon a platinum capsule heated to a white heat, and although this liquid ordinarily boils at a very low temperature there was no appearance of ebullition and the rate of evaporation was very slow. In this state some water poured into the sulphurous acid was instantly frozen. Faraday went even further, and by pouring on a red hot platinum capsule some ether and solid carbonic acid he formed a spheroidal mass which evaporated very slowly, but nevertheless solidified some mercury brought into contact with it.

In connexion with these experiments we may remark the very singular fact, that the skin of the hand, if slightly moistened, may be brought into contact with molten metal at a very high temperature without being sensibly affected or injured in the least. This may explain some of the tales which have reached us from the middle ages, in which accused persons went through the ordeal of fire with impunity.

129. The following are the experimental laws of this phenomenon.

1. It has been found by M. Boutigny that the lowest temperature of the hot surface capable of producing this state varies with the liquid, being higher for liquids of high boiling points. M. Marchand has shown that it also varies with the temperature of the projected liquid and with the nature of the surface.

2. The spheroid seems not to touch the surface. If this surface be a plane, M. Boutigny has found that the eye may see the light of a taper through the space between the liquid and the surface. He has also found that a drop of nitric acid has in this state no action on a silver or copper surface, nor one of dilute sulphuric acid on iron or zinc. Professor Poggendorff has also shown that if the hot plate be metallic and connected with one pole of a galvanic battery while the spheroid is connected with the other, no current will pass; thereby proving the interruption of contact between the spheroid and the plate.

3. M. Boutigny and M. Boutan have shown that liquids in the spheroidal state remain at a temperature inferior to that of ebullition.

130. An experiment made by M. Buff will serve to connect together the second and third of these experimental laws, and to show their dependence on one another. He placed a clean silver spoon filled with water over a lamp,

$$1000 \text{ BTU} = \int_T^{212}$$

say, if the vapour and air are quite independent of each other. For simplicity's sake we may imagine the second heating of the globe to take place not a very long time after the introduction of the water, in which case the vapour will not yet have penetrated to q (in Lamont's experiment there was no trace of vapour at this part of the apparatus). If these views be correct, there being no pressure of vapour at q , the pressure there will be entirely due to dry air. No doubt there is pressure of vapour in the globe K , but by this hypothesis it has no effect on the particles of dry air, and cannot therefore be communicated to q . The drop of quicksilver at q ought therefore to move, for a given heating of the ball, precisely the same distance whether the air of the globe be dry or whether it contain vapour.

Let us now suppose, instead of this hypothesis, that the air exerts a pressure upon the vapour and the vapour upon the air. Then the globe K will have a pressure of vapour corresponding to 40°C (104°Fahr.), which by Table I at the end of the volume is 2.16 inches; this has to be added to the pressure of dry air, and the sum will be communicated through the dry air of the tube to the quicksilver at q , which will, on this hypothesis, be pushed much farther when there is vapour than when there is only dry air. On the other hypothesis, however, as we have seen, the quicksilver will be pushed equally far in both cases. Now Lamont found that the quicksilver was pushed much farther when there were air and vapour together than when there was only dry air, and he therefore concluded that the first hypothesis is incorrect.

120. Various modes of vaporization. Our attention has hitherto been directed to certain laws which have no special reference to the particular modes in which vaporization is accomplished.

Let us now consider the peculiarities of these various modes. We have already (Art. 110) stated that there are three such—viz. *evaporation*, *ebullition*, and *vaporization in the spheroidal state*.

121. Evaporation. Evaporation denotes the quiet production of vapour at the surface of a liquid, and is subject to the following laws:—

1. It varies with the temperature.
2. It varies with the extent of surface exposed.
3. It goes on very rapidly in vacuo, but much more slowly in a space filled with air.
4. It goes on more rapidly in dry air than in air containing vapour.
5. It is assisted by any agitation tending to renew the particles of air over the evaporating surface.

The reason of the fourth and fifth laws is very evident. When vapour forms above the surface of a liquid in still air, it rises so slowly that the air above the liquid soon becomes saturated with vapour, or nearly so, and hence the evaporation, if not quite stopped, yet proceeds very slowly. But when new and comparatively dry particles of air are constantly brought into contact with the liquid the process is greatly facilitated.

This process is constantly going on in nature, and forms one of the means by which the surface of the earth is rendered fit for the maintenance of living beings; it is also of very extensive application in chemistry and in the arts, being employed to separate a volatile from a fixed substance.

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both sides of the surface as the temperature rose, showed itself to Dr. Andrews in the form of moving or flickering striae; and M. Amagat has seen it as an exceedingly fine rain upon the surface, both of vapour bubbles from below and of liquid droplets from above.

132. Sublimation. There are some solids which under ordinary circumstances of pressure appear to assume the gaseous state at once instead of passing through the intermediate state of liquidity. Of these arsenic and solid carbonic acid are examples. It is well known too that snow slowly evaporates, and thus to some extent appears to assume the gaseous form, even although the temperature is decidedly below that of the melting point of ice.

Again, some substances, such as chalk, are decomposed before fusion, the gaseous element going off. Nevertheless it has been found that if chalk be heated under intense pressure it melts and assumes the appearance of marble when it becomes solid.

Messrs. Ramsay and Young made some very interesting experiments in 1883 on the influence of temperature on the volatilization of solids, such as camphor, acetic acid, &c., from which it appears that solids have definite temperatures of evaporation or subliming points, just as liquids have definite boiling points, corresponding to definite pressures. At first sight it may appear that the analogy between solids and liquids cannot be carried farther, inasmuch as a boiling liquid appears to emit bubbles from its interior, while a subliming solid only emits matter from its surface. On reflection, however, we may be led to suppose that there is perhaps some breach of continuity equivalent to a surface at the points from which gas issues in a boiling liquid, and in this case the analogy between the behaviour of subliming solids and boiling liquids is very close indeed.

CONDENSATION OF VAPOURS AND GASES.

133. Distillation, or the condensation of vapours.

This process has already been described in Art. 117.

134. Condensation of gases. Sometimes gases are compelled to assume the liquid form by their affinity for some liquid. Thus, for instance, if ammoniacal gas is brought into contact with water it is immediately dissolved. The same result takes place with hydrochloric acid and other gases. This condensation of gas renders sensible a large quantity of latent heat, and it is therefore necessary to keep the vessel in which it takes place surrounded by cold water.

It is much more difficult to condense gases by themselves and without the aid of a chemical solvent. The auxiliaries employed in this condensation are, as might be imagined, pressure and cold. All gases have at length yielded to the joint effect of these two agents, but there were nevertheless six substances which until quite recently we could not obtain either in the liquid or the solid form—these being oxygen, hydrogen, nitrogen, nitric oxide, carbonic oxide, and marsh gas.

Faraday was one of the first who succeeded in liquefying gases by the joint application of cold and pressure. Others have since joined in these attempts, and carbonic acid gas is now condensed in large quantities, forming in this shape a very convenient source of cold. An instrument invented by Thilorier, somewhat modified, is very much used for the purpose of liquefying this gas; it acts on the following principle. The gas is generated in a strong iron vessel called the *generator*, into which the materials necessary for making the gas are put. This generator is connected with an equally strong iron vessel called the *receiver*, which is kept cool, and when sufficient gas has been generated it

condenses in the receiver. The two vessels are now separated and a fresh charge introduced into the generator, and the gas is condensed in the receiver as before, until at last a large quantity of liquefied gas has been obtained.



Fig. 32.

It will be seen from Fig. 32 that in the interior of the receiver there is a tube which descends below the level of the liquid. When the cock is opened the pressure of the gas drives the liquid with great force up the tube and out through the fine nozzle in which it terminates.

The liquid as it issues evaporates with such rapidity that part of it is frozen, and if on its way out it be made to play into a cylindrical box the solidified gas may be collected in the form of a snow-white powder. This powder evaporates very slowly, and may therefore by proper precautions be preserved for a considerable length of time. It may also be handled with impunity, and may even be laid upon the tongue without a disagreeable sensation of cold being produced, although the temperature of the solid is extremely low, perhaps even -77°C . The reason of this absence of the feeling of cold is want of contact between the two. If however this solid acid be mixed with ether, for which it has a great attraction, the mixture will now be in contact with the containing vessel, and will be felt to be intensely cold, while a rapid evaporation of carbonic acid will take place, thereby preserving the low temperature by drawing off the heat.

By means of a mixture of this description mercury in large quantities may readily be frozen. If the bath of carbonic acid and ether be placed in vacuo the evaporation is

accelerated, and a still greater degree of cold is produced : still lower temperatures being obtained by this method with other substances, as already mentioned in Art. 118.

PRESSURE AND DENSITY OF VAPOURS AND GASES.

135. Before discussing the laws which regulate the pressure of gases and vapours we must first of all bear in mind what takes place when we condense a gas or vapour into smaller volume. Let us suppose this condensation to be performed slowly and at a constant temperature. As it proceeds the pressure will of course increase, until at last, if the gas be condensable, liquid will begin to make its appearance. The pressure and density have now attained the greatest possible value which they can have for this temperature and for this kind of gas, and if the condensation be pushed further the only result will be the formation of more liquid, but without a further increase of pressure. Our inquiry must therefore be divided into two parts. We must consider, in the first place, the laws which regulate the pressure of gas or vapour not in contact with the liquid which produces it ; and, secondly, those which regulate the pressure of gas or vapour in contact with its own liquid.

136. Pressure of gas or vapour not in contact with its own liquid. We have already had occasion (Chap. IV. Art. 60) to advert to Boyle's law, which gives the relation between the pressure and volume of a gas, the temperature remaining constant, and we have seen that in this case the pressure varies inversely as the volume. We have also seen (Art. 62) that Charles and Gay-Lussac were the first to state the true connexion between the volume and temperature of a gas of which the pressure remains constant, and that this law may be expressed as follows :—

Let V denote the volume of a gas under given pressure at the temperature 0°C , then $V(1 + at)$ will be its volume under

the same pressure at the temperature $t^{\circ}\text{C}$, where $a = .00367$ nearly.

Neither of these laws is however absolutely correct under all circumstances. With regard to Charles' law it has been found by Regnault, as we have already seen (Art. 66), that it only holds absolutely in the case of a perfect gas, that is, of a gas very far removed from its point of maximum density; and in like manner Boyle's law ceases to be perfectly true when this same point is approached, for the density is then found to increase more rapidly than the pressure. But if the gas be sufficiently attenuated it is probable that both of these laws are exactly true, and in this case it is very easy to solve all problems in which it is sought to connect the pressure of a gas with its temperature and volume.

Thus, let $V_{(p, t)}$ denote the volume occupied by a gas at pressure p and temperature $t^{\circ}\text{C}$, and let it be required to find the volume of this gas at pressure p' and temperature t'° .

Calling $V_{(p, 0)}$ the volume at pressure p and temperature 0°C , we find, by Charles' law,

$$V_{(p, t)} = V_{(p, 0)}(1 + at); \quad \therefore V_{(p, 0)} = \frac{V_{(p, t)}}{1 + at}.$$

Also, by the same law combined with that of Boyle, we find

$$V_{(p', t)} = V_{(p, 0)}(1 + at') \frac{p}{p'};$$

and finally, substituting for $V_{(p, 0)}$ its equivalent $\frac{V_{(p, t)}}{1 + at}$, we

find

$$V_{(p', t)} = V_{(p, t)} \frac{1 + at'}{1 + at} \cdot \frac{p}{p'}.$$

Example. Let the volume of a gas be 5 litres at the pressure of 300 millimètres and at 15°C ; what will be its volume at the pressure of 350 millimètres and at 72°C ?

Here we have

$V_{(g, 0)} = 5$, $p = 300$, $p' = 350$, $t = 15^\circ$, $t' = 72^\circ$;
hence

$$V_{(g, t)} = 5 \times \frac{1 + .00367 \times 72}{1 + .00367 \times 15} \times \frac{300}{350} = 5.1355 \text{ litres.}$$

Other problems of a similar kind will easily suggest themselves.

137. Pressure of gas or vapour in contact with its own liquid. Since a gas or vapour in contact with its own liquid always possesses the greatest pressure possible at the temperature, there is consequently only one such pressure corresponding to each temperature; and hence for a given substance this maximum pressure will only vary when the temperature is made to vary, and it will vary in such a manner that the higher the temperature the greater the corresponding maximum pressure (Art. 112).

In mathematical language, the pressure of gas in contact with its liquid will be a function of the temperature; and what we wish to know is the nature of this function for each substance; that is to say, the relation in each case subsisting between such pressure and temperature. As this has been most extensively and accurately investigated for the vapour of water, we shall commence with it.

138. Pressure of aqueous vapour. Many experimentalists have engaged in this research, and yet it is only lately that great exactness has been obtained.

In 1823 the subject was referred to a Commission of the Academy of Paris, and the experiments undertaken in consequence were made by MM. Dulong and Arago.

The object of these was to determine the pressure of the vapour of water at high temperatures, and the experiments ranged between 1 and 24 atmospheres of pressure and between the temperatures 100° and 224°C .

About the same time the same subject was taken up by

a Committee of the Franklin Institute of Pennsylvania, their experiments ranging from 1 to 10 atmospheres.

The apparatus of the French Commission consisted of a manometer, or pressure measurer, having a detached column of atmospheric air cut off by mercury, which by its volume served to denote the pressure; the Commission having previously ascertained by direct experiment the correctness of Boyle's law for air up to a pressure of 27 atmospheres.

Very nearly the same apparatus was employed by the American Committee. Unfortunately, however, there was a considerable difference between the results of the two investigations. One cause of this discrepancy may have been the employment of mercurial thermometers composed of different kinds of glass, since we have seen (Art. 25) that at high temperatures the indications of two instruments of this kind, both accurately graduated but made of different kinds of glass, will not agree together. On this account Regnault resolved to make a full set of experiments on the subject, extending to high pressures but also embracing low ones, and he completed these in 1862 with very satisfactory results.

139. Regnault divided his research into three parts.

The first of these relates to his experiments on the pressure of aqueous vapour at low temperatures; that is to say, from -32° to $+50^{\circ}\text{C}$.

The second part comprehends all his experiments at higher temperatures, or from 50° to 230°C .

Finally, in his third part he treats of the *graphic representation* of his experiments, and discusses various *formulae of interpolation*.

In the first place, as regards his experiments at low temperatures, Regnault employed various methods, and even repeated those made use of by former experimentalists,

in order, as he tells us, to see if when used with proper precautions they would all lead to the same result; and if this be not the case, to point out by direct experiment the causes of error in the defective methods.

The general plan underlying the various methods made use of by him in this branch of his investigation is that of comparing together two barometers placed side by side, one having a dry vacuum chamber, and the other a chamber filled with the vapour of water at a determinate temperature; the difference between the heights of the two giving the pressure of aqueous vapour at the temperature of the experiment. He found that when sufficient precautions were adopted the various methods employed by him agreed together very well.

140. In the second part of his research, which had reference to high temperatures, Regnault employed another kind of apparatus, founded on the principle that the vapour of water boiling in a large space filled with air has a pressure equal to the atmospheric pressure.

In order to secure all the advantages of this method Regnault constructed the following apparatus. A strong retort *A* (Fig. 33) contains the water to be heated, and has arrangements for holding four mercurial thermometers, two of them being plunged in the water, and two in the vapour of water: these arrangements are such that the bulbs of the thermometers are not exposed to the pressure of the vapour. In order to ensure correctness Regnault employed an air thermometer in addition to the mercurial ones. The retort *A* is connected by means of a long neck *CC* with a balloon or reservoir *B*, into which air may be pumped or from which it may be extracted, so that the internal pressure of the air may be regulated at pleasure. The balloon is enclosed in water of the temperature of the surrounding medium, by which means change of pressure due to change

of temperature of the balloon is avoided. The neck *CC*, connecting the balloon *B* with the retort, is kept cool by a stream of water constantly flowing through a cylinder which surrounds it. By this means the vapour is condensed

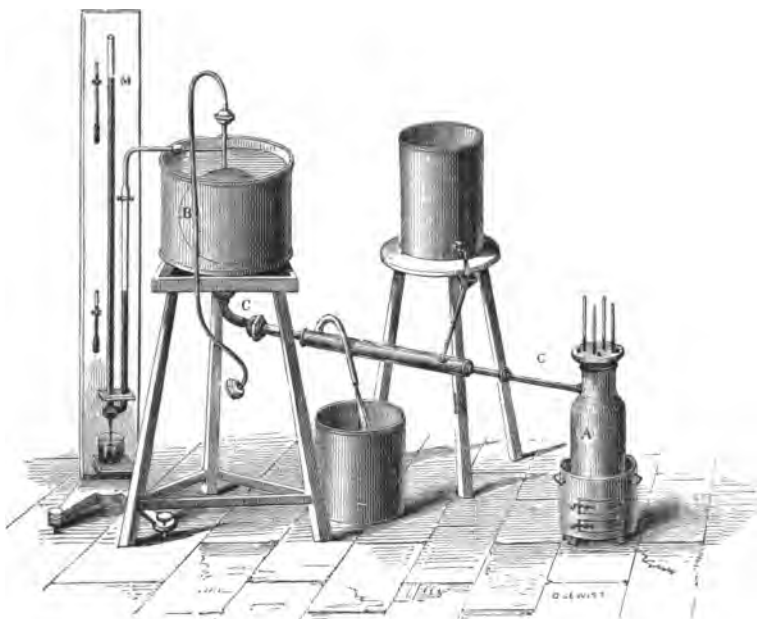


Fig. 33.

as fast as it is formed, and trickles back into the retort, its pressure being equal to that of the artificial atmosphere in *B*.

It only remains to state that the air of the balloon *B* communicates with one column of a manometer *M*, the other column being open to the atmosphere. It is evident from the arrangement in the figure that the pressure of air in *B* is equal to that of the external atmosphere *plus* or

minus (as the case may be) the pressure of a column of mercury equal in length to the difference between the levels of this fluid in the two limbs of the manometer. By this method Regnault was enabled to measure accurately the temperature of the vapour, and also to keep the pressure of the artificial atmosphere (and in consequence the temperature of ebullition) very nearly constant; lastly, this pressure might be accurately measured by means of the attached manometer.

141. The third part of Regnault's memoir relates to the *graphic representation* of his experiments, and to *formulae of interpolation*. The following considerations will suffice to show the necessity for this.

There are two kinds of errors which make their appearance in physical research. The first of these is due to a defect in the process employed, or to a defect of the observer. Thus in the particular problem under consideration, namely, that of finding the maximum pressure of aqueous vapour corresponding to a given temperature, the methods employed by the earlier observers were defective to some degree. But the course pursued by Regnault in his investigation got rid of this source of error to a very great extent: for he worked out the various methods of his predecessors after having discovered and corrected their defects, and he then found that the results obtained agreed very well together. We may therefore imagine that in his experiments errors due to defective apparatus or observation have been to a very great extent eliminated. There is however another description of error which cannot be entirely got rid of. If, for instance, we make the same observation with the same instrument under the same conditions several times in succession, we shall find that none of the results obtained agree exactly together, although they all lie within a very narrow range.

Under these circumstances men of science are agreed upon a certain mathematical treatment, which when applied to a set of observations yields the best result; and it will always be found that results thus obtained from sets of observations agree together much better than the results of individual observations.

We see now the distinction between the two classes of errors. The one is an error of apparatus or observer that affects all the observations alike, and which cannot be got rid of by multiplying observations; the other is an error which will manifest itself with the most perfect instruments, but which may be got rid of by multiplying observations.

Let us now return to the case in hand, and suppose that Regnault had found a number of values for the pressure of aqueous vapour at 100°C , all slightly different from one another; having previously rendered his apparatus and method of observing as accurate as he could, he would then group them together so as to obtain the most probable result. The same thing will apply to an observation at any other temperature, so that at last we may suppose that the observer has obtained the most probable values of the pressure of aqueous vapour at the various temperatures of experiment. These results are not *absolutely* free from either of the two kinds of error we have described, but only as nearly free as he can get them. It will however be borne in mind that in this process, as we have described it, each different temperature is considered apart by itself, and the result obtained gives the most probable value of the pressure for any given temperature, the observations for this temperature being considered as quite unconnected with those for any other temperature. The question then arises, can we combine together and compare the various values thus obtained for different temperatures so as to make them mutually

correct each other's errors? This is to a great extent accomplished by the method of graphic representation.

Let us, for instance, reckon the temperatures along a line of abscissæ, after the manner represented in the figure, and raise at the various temperatures of experiment ordinates proportional to the observed pressures; and finally, connect the extremities of our ordinates together by a line. We shall find that this line, while it approaches very nearly to a regular curve, has yet a great many sinuosities, and

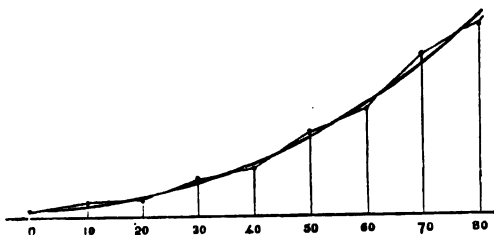


Fig. 34.

a little consideration will convince us that these irregularities do not denote any law of nature, but are merely due to the residual error in our observations; and that the most probable line denoting the true law of nature, which we are seeking, will be a curve passing midway between these points and leaving as many above it as below. Now suppose that when we have traced such a curve the eye yet detects an abnormal bend of considerable extent at some region where we can imagine no natural cause for any deviation in the regular sweep of the curve, then we may very justly suspect that some error has crept into our determinations at that region, and we ought, if possible, to repeat our experiments.

We thus see the value of this process in detecting errors,

and it is one which is very generally employed by experimentalists.

In the present case, Regnault, having constructed such a curve with great care, adopted it as the most probable representation of the law connecting together the pressures and temperatures of aqueous vapour, as shewn by the experiments which he had made.

142. After we have constructed a curve of this kind, something more yet remains to be done in order to make the experiments as serviceable as possible. For this purpose it is necessary to know the pressure for each exact degree from -30° to 230°C , and even for each tenth of a degree throughout part of this range. This may of course be determined at once from the curve by raising ordinates at the points denoting these various temperatures and measuring their lengths with great exactness. In practice, however, another method is preferred. Our observations have furnished us with a curve, but we do not know the exact equation between the abscissæ and ordinates which represents this curve; if we knew this equation we might at once find the ordinate corresponding to any abscissa, that is to say, the pressure corresponding to any temperature. But while we are ignorant of the exact equation we may try different equations, and we shall no doubt be able to find formulæ that will represent the progress of the curve with very great exactness, one formula suiting one part best and another another part. And thus by means of these, which are called formulæ of interpolation, we may readily find the value of the pressure corresponding to each exact degree and decimal of a degree between the limits of the experimental research.

143. **Correction for latitude and height above sea level.** In the results of Regnault's experiments the pressure is expressed in the length of the column of pure

mercury which it will sustain, the mercury being at 0°C , at the latitude of Paris ($48^{\circ} 50'$), and at the height of 60 mètres above the level of the sea. But we have already remarked (Art. 21) that the absolute pressure of a column of mercury of given length varies with the latitude, and we may add that it varies, although but slightly, with the height of the place of observation above sea level; in fact its absolute pressure varies with the intensity of gravity at the place of experiment. If, therefore, Regnault had made his experiments at another latitude and height he would have obtained lengths of the mercurial column to denote his pressures different from those which he obtained in Paris.

The following is the formula by means of which the results at one latitude and height are made comparable with those at another. Let g denote the intensity of gravity at the latitude 45° and at the level of the sea, R the mean radius of the earth = 6366198 mètres = 20886852 feet; also let λ' denote the latitude of the place of observation, and h' the height above the level of the sea; then if g' denote the intensity of gravity at this locality, we have—

$$g' = g \left\{ 1 - .002837 \cos 2\lambda' \right\} \frac{R^2}{(R + h')^2}$$

$$= g(1 - .002837 \cos 2\lambda' - .000000314h')$$

approximately. Hence the intensity of gravity at Paris (latitude $48^{\circ} 50'$) at the height of 60 mètres above the level of the sea will be denoted by

$$g\{1 - .002837 \times (-.1334) - .000000314 \times 60\}$$

$$= g \times 1.000360.$$

Also the intensity of gravity at Greenwich near London (latitude $51^{\circ} 28'$) at the level of the sea = $g \times 1.000635$.

We see now that the pressure denoted by 760 millimètres or 29.922 inches of mercury at 0°C at Paris will correspond to $29.922 \times \frac{1.00036}{1.000635} = 29.913$ inches of mercury at 32° Fahr. at London, and this is in accordance with what we have already stated (Art. 21).

If, therefore, we adhere to centigrade degrees it is very easy to convert Regnault's table into one expressing the pressure of vapour at any temperature in inches of mercury at 0°C at the place of observation; but if we use degrees Fahrenheit we shall find that Regnault's tables do not give us the pressure at our precise points of temperature, and we shall have to calculate these as Regnault himself did, by adapting his formulæ of interpolation to our case. In this adaptation it must be borne in mind that 212° Fahr. is not *exactly* 100°C.

The Rev. Robert Dixon, in his work on Heat, has made the requisite adaptation with great care, and we cannot do better than present to our readers in an abbreviated form the tables he has calculated.

They are adapted to the latitude of Dublin, viz. 53° 21', which will answer very well for any station in Great Britain or Ireland.

These tables, along with an abbreviation of Regnault's table, will be found at the end of this work; they comprise—

Table I. Shewing the pressure of aqueous vapour in inches of mercury at the latitude 53° 21' for each degree Fahr. from -30° to +432°.

Table II. Shewing the pressure of aqueous vapour in inches of mercury at the same latitude from 0° to 100° Fahr. for every two-tenths of a degree.

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Table III. Shewing the pressure of aqueous vapour in millimètres of mercury at the latitude of Paris ($48^{\circ} 50'$) for each degree Centigrade from -32°C to $+230^{\circ}\text{C}$.

144. **Pressure of other vapours.** Signor Avogadro, M. Regnault, and others have determined the pressure of the vapour of mercury at various temperatures, but their results can only be considered approximative. Regnault has also determined the pressure of other vapours at various temperatures, and the following table gives the results of some of his experiments.

Pressure of vapour in millimètres of mercury.

Temp. Cent.	Alcohol.	Ether.	Sulphuret of Carbon.	Chloroform.
-20	3.34	68.90	47.30	
-15	5.10	89.31	61.64	
-10	6.47	114.72	79.44	
-5	9.09	146.06	101.29	
0	12.70	184.39	127.91	
+5	17.62	230.89	160.01	
10	24.23	286.83	198.46	
15	32.98	353.62	244.13	
20	44.46	432.78	298.03	160.47
25	59.37	525.93	361.13	200.18
30	78.52	634.80	434.62	247.51
35	102.91	761.20	519.66	303.49
40	133.69	907.04	617.53	369.26
45	172.18	1074.15	729.53	446.01
50	219.90	1264.83	857.07	535.05
55	278.59	1481.06	1001.57	637.71
60	350.21	1725.01	1164.51	755.44
65	436.90	1998.87	1347.52	889.72
70	541.15	2304.90	1552.09	1042.11
75	665.54	2645.41	1779.88	1214.20
80	812.91	3022.79	2032.53	1407.64
85	986.40	3439.53	2311.70	1624.10
90	1189.30	3898.26	2619.08	1865.22
95	1425.13	4401.81	2966.34	2132.85
100	1697.55	4953.30	3325.15	2428.54
105	2010.38	5556.23	3727.19	2754.03
110	2367.64	6214.63	4164.06	3110.99
115	2773.40	6933.26	4637.41	3501.03
120	3231.73	7719.20	5148.79	3925.74

145. Influence of the change of condition from liquid to solid on vapour pressure. Experiments were made by Gay-Lussac and Regnault from which it was concluded that *the passage of a substance from the liquid to the solid state is without influence upon the vapour densities.* Certain considerations (Arts. 447-452) lead us however to infer that in the curve which represents correct observations on the pressure of aqueous vapour there is a slight break near the freezing-point; and a close examination of Regnault's results really confirms this view, as do recent observations by Professors Ramsay and Young.

146. Dalton's hypothesis regarding vapour pressures. Dalton supposed that the pressures of all vapours would be equal at equal distances from their respective boiling-points. Thus, for example, water boils at 212° Fahr. and alcohol at 173° . Of course at these temperatures the pressures of the vapours are equal, being represented by one atmosphere, or 30 inches of mercury. According to Dalton the pressures of these two vapours will also be equal at

$$212 - 10 = 202^{\circ} \text{ and } 173 - 10 = 163^{\circ}.$$

The hypothesis of Dalton does not generally hold, but for short distances on either side of the boiling-point it holds approximately in a large number of instances¹.

147. Density of gases and vapours. When substances are compared together in the state of gas at the same temperature and pressure, a very simple relation is found to subsist between their density and their combining chemical equivalent. This was first discovered by Gay-Lussac, who found that *when gases or vapours combine together, the volumes in which they combine bear a very simple ratio to one another.* The following table, kindly furnished by

¹ Dr. Carnelly has recently published in two large volumes very complete tables of melting and boiling points and likewise of vapour pressures.

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Dr. Williamson, will serve to illustrate this law, which is generally called the law of volumes.

<i>Vapour volume of compounds.</i>	<i>Vapour volume of elements liberated from them.</i>
Hydrochloric acid (HCl) 2 vols. ...	1 vol. hydrogen + 1 vol. chlorine.
Hydrobromic acid (HBr) 2 vols. ...	1 vol. hydrogen + 1 vol. bromine.
Hydriodic acid (HI) 2 vols. ...	1 vol. hydrogen + 1 vol. iodine.
Steam (H ^o O) 2 vols. ...	2 vols. hydrogen + 1 vol. oxygen.
Ammonia (NH ³) 2 vols. ...	1 vol. nitrogen + 3 vols. hydrogen.

We see from this table that equal volumes of chlorine and hydrogen, for instance, combine together without change of volume to form hydrochloric acid gas, which contains one atom of hydrogen united to one of chlorine. Equal volumes of chlorine and hydrogen contain therefore an equal number of atoms of these elements.

There are thus three laws which bear immediately upon the density of gases. 1. The above law of volumes, in which the density of a gas at a *given temperature and pressure* is shewn to depend upon its chemical constitution; 2. Boyle's law, in which the density of a gas of a *given constitution and temperature* is shewn to depend upon its pressure; 3. Charles' law, in which the density of a gas of a *given constitution and at a given pressure* is shewn to depend upon its temperature.

148. Many experiments have been made with a view to determining whether these three laws hold for all gases and vapours, and we shall now very briefly indicate the various methods pursued in these investigations.

In the first place, Gay-Lussac's method in his researches consisted in ascertaining the volume occupied by a known mass of liquid when entirely converted into vapour at a certain temperature and pressure.

It is, however, essential to this method that the whole of the liquid should be converted into vapour, and hence it is inapplicable to a gas at its maximum density and in

contact with its own liquid. It only applies to cases where the density is considerably inferior to that of saturation. No doubt the density of saturation might be calculated from an experiment of this kind, if we supposed Boyle's law to hold good ; but one great object of such experiments is to determine whether this law holds accurately for gases near their point of saturation.

In order to obviate this objection M. Despretz introduced a method which consists in filling with gas or vapour at different temperatures and pressures a balloon of known weight screwed on the top of a barometer tube.

Afterwards Dumas, in order to experiment upon gases that act upon mercury, and to obtain results at high temperatures, used a glass balloon *G* drawn out to a fine point (Fig. 35), which was first of all well dried and weighed, the temperature and pressure of the air being at the same time accurately noted. The balloon was then slightly warmed and its point immersed in the liquid of which it was wished to find the vapour density, and as the balloon cooled a small quantity of this liquid entered it. The balloon was then heated in a bath to a point somewhat above the boiling-point of the liquid which it contained, and kept there until there was only vapour in the balloon ; it was



Fig 35.

then hermetically sealed, the temperature of the bath and the barometric pressure of the air being both accurately noted. Finally, it was once more weighed when cool.

Dumas thus obtained two weighings, one of the balloon filled with air of known pressure and temperature, and the other of the same balloon filled with vapour of known pressure and temperature, from which he was enabled to determine the density of the vapour.

More lately Regnault has made several series of experiments on this subject.

1. His first series was on the density of aqueous vapour *in vacuo* at the temperature of boiling water and under a pressure not exceeding half an atmosphere, and he found that both Boyle's and Charles' laws were applicable within the limits of his experiments; but when the pressure approached more nearly to its maximum, he found that the density increased more rapidly than the pressure.

2. His second series was on the density of aqueous vapour *in vacuo* at temperatures not very far removed from that of the surrounding medium, and from these he concluded that the density of aqueous vapours *in vacuo* and under feeble pressures may be calculated according to Boyle's law, provided that the fraction of saturation does not exceed 0.8, but that this density is notably greater when we approach more nearly to the state of saturation. He adds, however, that this latter circumstance may be owing to one or both of two causes: either aqueous vapour really suffers an anomalous condensation on approaching its point of saturation, or a portion of the vapour remains condensed on the surface of the glass, and does not assume the aëriform state until the mass of vapour is at some distance from the point of saturation.

3. Regnault has also examined the density of aqueous vapour *in air* at its maximum value for the temperature of experiment between the limits 0° and 25°C, and he concludes that the density of aqueous vapour in air, in a state

of saturation and under feeble pressures, may be calculated, without much error, from Boyle's law.

Messrs. Fairbairn and Tate have made experiments to determine the density of steam at different temperatures, and to find the law of expansion of superheated steam.

The general plan of their method of ascertaining the density of steam consists in vaporizing a known weight of water in a large glass globe with a stem, of known capacity and devoid of air, and observing the exact temperature at which the whole of the water is just vaporized.

In the following table these authors exhibit the relation between the specific volume, pressure, and temperature of saturated steam as determined from their experiments. Specific volume denotes the number of times the volume of steam exceeds the volume at 39°·1 Fahr. of the water from which it is raised.

Pressure in inches of mercury.	Maximum temperature of saturation, in degrees Fahr.	Specific volume of steam.
5·35	136·77	8275·3
8·62	155·33	5333·5
9·45	159·36	4920·2
12·47	170·92	3722·6
12·61	171·48	3715·1
13·62	174·92	3438·1
16·01	182·30	3051·0
18·36	188·30	2623·4
22·88	198·78	2149·5
53·61	242·90	943·1
55·52	244·82	908·0
55·89	245·22	892·5
66·84	255·50	759·4
76·20	263·14	649·2
81·53	267·21	635·3
84·20	269·20	605·7
92·23	274·76	584·4
90·08	273·30	543·2
99·60	279·42	515·0
104·54	282·58	497·2
112·78	287·25	458·3
122·25	292·53	433·1
114·25	288·25	449·6

With regard, in the next place, to superheated steam, the results of these experiments shew that for temperatures within about ten degrees from the maximum temperature of saturation, the rate of expansion on account of heat greatly exceeds that of air, whereas at higher temperatures from this point the rate of expansion approaches that of air, so that as the steam becomes more and more superheated, the coefficient of expansion approaches that of a perfect gas, while at or near the maximum temperature of saturation the coefficient of expansion greatly exceeds that of a perfect gas.

Dr. Hermann Herwig has also made an elaborate investigation on the conformity of vapours to Boyle's and Charles' laws. He states that whenever a sensible deviation of purely saturated vapour from the gaseous state has taken place, a very considerable elevation of temperature is necessary in order by superheating a constant volume to make it pass into the gaseous condition.

We thus perceive that near their points of saturation gases and vapours would appear to depart both from Boyle's and from Charles' law, while probably if the pressure under which they exist be far inferior to that of saturation these laws are obeyed.

Generally speaking, we may presume that *the three laws which we have before enunciated as regulating gaseous density (namely, the law of volumes, Boyle's law, and Charles' law) hold accurately only in the case of perfect gases.*

149. Regnault has furnished us with the following determination of the mass of a litre of the most important gases under standard conditions.

Mass of one litre (61.02538 cubic inches) of Gases at 0°C under the pressure of 760 millimètres of mercury at 0°C at Paris (29.913 inches of mercury at 32° Fahr. at London).

Name of gas.	Specific gravity.	Mass in grammes.
Air	1.0000	1.293187
Oxygen	1.1057	1.429802
Hydrogen	0.0693	0.089578
Nitrogen	0.9714	1.256167
Carbonic acid. . . .	1.5291	1.977414

We have also the following specific gravities of vapours.

Air	1.0000	
Vapour of water . . .	0.6235	Gay-Lussac and Thenard.
„ alcohol	1.6133	Gay-Lussac.
„ ether	2.5860	Gay-Lussac.

150. Hygrometry. Hygrometry is that branch of science which treats of the state of the air with regard to moisture. As this is one of the elements which form the climate of a place, and as the human body is very much affected by the hygrometric state of the air, the subject is one of much practical importance.

There are several facts regarding the vapour present in the air which it is very desirable to know.

151. One of these is its Pressure. Suppose that we were to isolate in a vessel a cubic foot of air, allowing it to remain at its present temperature and pressure, and then to introduce into the vessel containing it a substance which absorbs moisture; the air by this means will be rendered dry, and its pressure will be diminished by an amount representing the pressure of aqueous vapour present in the air.

It is of importance to know what this pressure is, for upon this, among other things, depends the behaviour of the air when it is cooled down. If, for instance, at

the higher temperature there be present nearly as much aqueous vapour as the air can contain at that temperature, then if the air be cooled down only a few degrees, some of this vapour will be deposited in the liquid or solid state. The temperature at which this takes place is called the *dew-point*. We thus see that if the pressure of vapour in the air at its existing temperature be great the dew-point will be high, but if this pressure be small, the dew-point will be low in the thermometric scale.

152. Another object of research is the relative humidity of the air. Of course all substances exposed to the air will be affected by the deposition of moisture when the dew-point is reached ; but many substances will be affected long before this takes place : our bodies, for instance, will experience the wetness of the air long before. On the other hand, if the present temperature be far above that of deposition, we pronounce the air dry. It ought here to be observed that the sensation of dryness or wetness does not depend upon the *absolute* amount of aqueous vapour present in one cubic foot of air. For if the temperature be very low, although the air may not contain much aqueous vapour, yet this vapour may approach very nearly to the maximum amount which can be retained at the temperature, and the air will be pronounced wet. But if the very same mixture of air and vapour be heated up many degrees, the vapour will represent only a small fraction of the total amount which can be retained at the higher temperature, and hence the air will feel very dry. If this high temperature be produced by a stove, it may even be necessary to place near the stove a vessel containing water in order to increase the amount of aqueous vapour present in the air.

We see now what is meant by the dryness or wetness of the air, and all that remains is to express it numerically. This is done by the conception of *relative humidity*, which

may be thus defined. *Relative humidity* is the fraction expressing the ratio of the amount of vapour actually present in the air at a given temperature to the greatest amount of vapour which it can contain at that temperature. The greatest amount, representing complete saturation, is generally reckoned equal to 100, and on this principle 50, 40, 30, &c. will denote that the air contains 50, 40, 30, &c. per cent. of the maximum amount which can be contained at that temperature.

153. The mass of vapour present is another object of interest. In order to know completely the state of the air it is necessary to know the mass of vapour present in a given volume of air, and also the entire mass of a given volume of air, or its specific gravity. This last element is necessary on another account, for a body weighed in air is lighter than if weighed *in vacuo* by the weight of its own bulk of air; in very delicate weighings, therefore, it is necessary to find the exact mass of the air displaced by the body; and in order to obtain this information it is not sufficient to know the temperature and pressure of the air, but we must also know the mass of vapour contained in a given volume of air.

Finally, for meteorological purposes it may be desirable to investigate what may be termed the *hygrometric quality* of the air. This may be defined to be the ratio of the mass of one cubic foot of air to that of the aqueous vapour present in it. Since dry air and aqueous vapour are affected by temperature and pressure according to the same laws, it is evident that the *hygrometric quality* will not vary unless there be either evaporation, precipitation, or mixture going on in the air. We may thus probably expect that the *hygrometric quality* of a body of air is less easily altered than either its temperature or pressure.

By testing the quality of the air at various points of the

earth's surface we may therefore possibly obtain an amount of physical knowledge of the motion of our atmosphere comparable to that which we have obtained regarding oceanic currents from observations of sea-temperature and saltness.

154. Having now mentioned the objects sought in hygrometry, let us proceed to describe shortly the various instruments made use of in this science. We may state at the commencement that there are various means of ascertaining in a general way the dryness or wetness of the air. We may, for instance, use some substance which has a great affinity for water and readily deliquesces. Such a substance, if the air be very dry, will remain a long time comparatively unaffected, but if the air be moist it will rapidly deliquesce. In the next place, various substances have the property of becoming elongated when moist and of contracting again when dry; a hair, for instance, possesses this property, and Saussure has used it in his hair hygroscope. Other bodies, such as catgut, untwist when moist and twist when dry; and a toy has been made in which there are two figures, a man and a woman, suspended by catgut in such a manner that the man comes out when the air is wet and the woman when it is dry. All these methods, however, *indicate* rather than *measure* the hygrometric state of the air—they are *hygroscopes* rather than *hygrometers*—and we proceed from these to instruments by which the state of the air with regard to moisture may be determined with precision.

155. Dew-point instruments. **Daniell's dew-point hygrometer.** This instrument (Fig. 36) is composed of two glass bulbs. The one *A* is more than half filled with

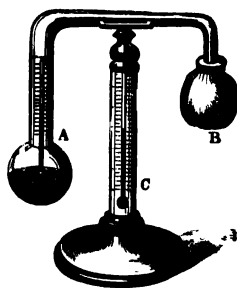


Fig. 36.

ether, and contains a delicate thermometer plunged in the ether; the space above is void of air and of everything but the vapour of ether. The bulb *B* is covered with some fine fabric, such as muslin, upon which ether is dropped; the evaporation of the ether produces intense cold, in consequence of which the ether vapour inside *B* is rapidly condensed, and of course the ether in *A* as rapidly evaporates. The evaporation of the ether at *A* cools the bulb until the air in contact with it sinks below the dew-point. Dew is therefore deposited on the outside of *A*, which is made of black glass in order that this deposition may be more readily observed. At the moment of deposition the thermometer in *A* is read. When the dew disappears, as the temperature rises, the same thermometer is also read, and the mean

of these two readings is taken to indicate the dew-point. The thermometer *C* gives the temperature of the air.

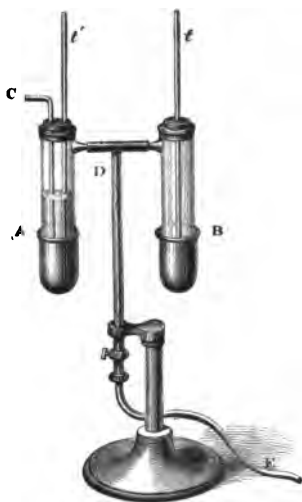


Fig. 37.

156. Regnault's dew-point hygrometer. Regnault has invented a dew-point hygrometer which is free from some of the objections to which Daniell's is liable. It consists (Fig. 37) of two tubes of polished silver having glass tubes fixed to them. The tube *A* is half filled with ether. It contains a thermometer *t'* with its bulb in the ether, and also a fine glass tube *C* open at both ends, the

extremity *C* being open to the atmosphere, and the other open end being plunged below the ether of *A*. The bulb *B*

also contains a thermometer t , the object of which is to indicate the temperature of the air. There is a communication between the air in A and the tube DE , and to the end E of this tube is attached an aspirator. By means of this aspirator the air from A is drawn through the tube DE , and its place supplied by new air entering at C and bubbling up through the ether. This continual current of air passing through the ether causes it to evaporate rapidly, and a diminution of temperature is thus produced, until at last dew is deposited on the polished silver of A ; the exact moment of deposition may easily be observed, and if the temperature of t' be immediately noticed, we obtain the dew-point with great exactness, since the agitation of the ether renders it certain that the temperature of this thermometer is precisely the same as that of the polished silver. The moment of the disappearance of the dew may also be noted, but we have not in this case the same certainty that the thermometer and the polished silver are of the same temperature.

157. Wet and dry bulb hygrometer. This instrument was devised by Mason, and consists of two thermometers (Fig. 38) placed alongside of each other, one having a dry bulb and the other a bulb covered with muslin, kept moist by an arrangement similar to that in the figure.

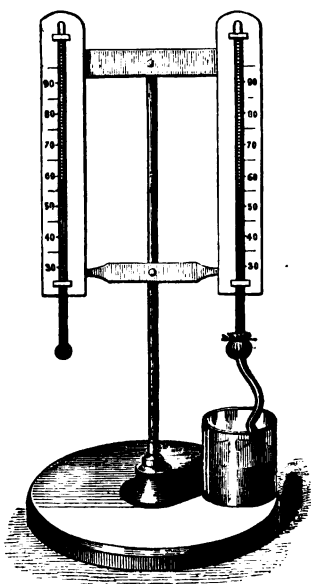


Fig. 38.

Owing to the evaporation from the latter its temperature will be generally below that of the former, and this difference will be greatest when the air is very dry, while in a very wet atmosphere the two temperatures will nearly coincide ; the reason of this being that evaporation (Art. 121) is more rapid in dry than in moist air.

It might at first sight appear that the difference between the two instruments would depend, not only on the dryness of the air, but also upon its velocity, since we have seen (Art. 121) that agitation of the air is favourable to evaporation. Unquestionably the withdrawal of heat by evaporation is greater when there is a current of air, but then it must be remembered that the difficulty of keeping a thermometer at a temperature below that of the air is increased by the same cause and very nearly in the same proportion.

This arrangement may be advantageously employed as a simple method of ascertaining the hygrometric state of the air with considerable accuracy, and for this purpose a formula, devised by Dr. Apjohn, is employed.

This formula is founded on the following assumptions. It is assumed, in the first place, that the particles of air in contact with the wet bulb are reduced by its cooling agency from the temperature of the surrounding air to that of the wet bulb, and that in consequence they give up a certain amount of heat to the wet bulb. On the other hand, the evaporation of the moisture around the wet bulb drains it of heat. Now, when the temperature of the wet bulb has become constant, the heat which it receives from the air must be precisely equal to that which is taken from it by the evaporation.

It is furthermore assumed that the particles of air surrounding the wet bulb are saturated with vapour. By means of these assumptions it is possible to find the hygrometric state of the air. In order to prove this let us

suppose that d denotes the difference in degrees Fahrenheit between the temperature of the air and that of evaporation, or, in other words, between the dry and wet bulb; also let f' denote the maximum pressure of vapour corresponding to the temperature of the wet bulb, while f'' denotes the pressure of vapour present in the air which we wish to find, and h denotes the height of the barometer in inches.

Knowing the specific heat of air Apjohn found that 4195 grains of air will, in cooling through d degrees, give out sufficient heat to vaporise d grains of vapour. If, therefore, in the course of a certain time 4195 grains of air have been cooled down through d degrees by the wet bulb, they must have imparted to it a quantity of heat which (since its temperature remains constant) must have been wholly spent in evaporating d grains of vapour.

Now, this mass of air is also supposed to have become saturated with vapour at the temperature of the wet bulb. But in order to be saturated at this temperature the air must (Art. 149) contain

$$4195 \times 0.6235 \times \frac{f'}{h} = 2616 \times \frac{f'}{h}$$

grains of vapour. Of these we have seen that d grains have been supplied by the wet bulb, so that the air must have had in it previously a quantity of vapour equal to

$2616 \times \frac{f'}{h} - d$. But the unknown vapour pressure of the air is supposed to be f'' , and hence the mass of vapour originally present in this amount of air must have been $2616 \frac{f''}{h}$. We have thus obtained two expressions for the

mass of vapour originally present in this air; that is to say,

$$2616 \frac{f'}{h} - d = 2616 \frac{f''}{h},$$

or approximately

$$f'' = f' - \frac{dh}{2610} = f' - \frac{d}{87} \times \frac{h}{30},$$

by which means f'' may be easily found. For temperatures of evaporation below 32° Fahr. the formula becomes

$$f'' = f' - \frac{d}{96} \times \frac{h}{30},$$

the latent heat of evaporation being here somewhat different.

Having found f'' , or the pressure of the vapour present in the air, we have only to look in our table for the temperature of which the saturation pressure is f'' in order to obtain the dew-point. Now it has been found, as the result of numerous experiments, that the dew-points obtained by this simple method agree very well with those determined by *direct observation* with Daniell's or Regnault's dew-point hygrometer.

158. Mass of vapour present in air. Specific gravity of air. We can easily calculate the mass M of a litre of dry air at temperature $t^\circ\text{C}$ and pressure P millimètres by the formula (see Arts. 136, 149)

$$M = 1.293187 \times \frac{P}{760} \times \frac{1}{1 + .00367 \times t} \text{ grm.}$$

In like manner if we wish to know the mass M' of a litre of aqueous vapour at temperature t' and pressure P' , we have (Art. 149)

$$M' = 0.6235 \times 1.293187 \times \frac{P'}{760} \times \frac{1}{1 + .00367 \times t'} \text{ grm.}$$

Suppose now it is wished to know the mass of one litre of air at a temperature 15°C and pressure equal to that of 750 millimètres of mercury reduced to 0°C at Paris, the dew-point being 10°C .

Production and Condensation of Vapour. 165

By Table III at the end of this work we find that the vapour pressure corresponding to 10°C is 9.165 millimètres. Hence 740.835 millimètres will represent the pressure of dry air, and 9.165 millimètres the vapour pressure at the time of observation. Now the mass of the dry air in one litre will be—

$$M = 1.293187 \times \frac{740.835}{760} \times \frac{1}{1 + .00367 \times 15} \text{ grm.} = 1.19480 \text{ grm.};$$

also the mass of vapour in one litre will be—

$$M' = 1.293187 \times .6235 \times \frac{9.165}{760} \times \frac{1}{1 + .00367 \times 15} \text{ grm.} = 0.00922 \text{ grm.}$$

Hence the whole mass of the moist air will be 1.20402 gramme.

159. Correction for weighing in air. This will be best understood by an example. Suppose, for instance, that a substance of the approximate specific gravity 2.5 weighs 100 grammes in the air of which the specific gravity was determined in the last article, and that the approximate specific gravity of the weights against which it is compared is 9.0.

Now since the specific gravity of the substance is 2.5, we see from Art. 76 that the mass of a cubic decimètre or litre of the substance will be 2.5 kilogrammes, or 2500 grammes; and hence, since it weighs only 100 grammes, its volume will be $\frac{100}{2500} = .04$ litre.

In like manner the volume of the weights against which it is weighed will be $\frac{100}{9000} = .01$ litre.

The mass of air displaced by the substance will therefore be

$$1.20402 \times .04 \text{ grm.} = .04816 \text{ gramme,}$$

and that displaced by the weights will be

$$1.20402 \times .01 \text{ grm.} = .01338 \text{ gramme.}$$

Hence the substance will weigh heavier *in vacuo* than in air by $\cdot 04816$ gramme.

In the next place it must be remembered that the *real* mass of the body is somewhat less than 100 grammes, for the weights against which it is balanced denote 100 grammes *in vacuo*, and hence in air they will denote

$$100 - \cdot 01338 = 99\cdot 98662 \text{ grammes, nearly.}$$

Therefore the true mass of the body will be

$$99\cdot 98662 + \cdot 04816 = 100\cdot 03478 \text{ grammes.}$$

CHAPTER VIII.

Effect of Heat upon other Properties of Matter.

180. In the preceding chapters we have described the action of heat upon bodies, chiefly as it affects their volume and condition; but this agent also affects them in many other ways, and to these we shall now allude: but in the first place it may be well to recapitulate very shortly the leading results of the preceding articles.

We have seen that as the temperature of a solid rises it almost invariably expands in volume, and also that the coefficient of expansion is greater at a high temperature than at a low one. If we continue to heat the solid it will ultimately assume the liquid state. In some bodies this change of state takes place very abruptly, but in others very gradually, so that they require a very considerable range of temperature in order to complete the change and become perfectly liquid. Sealing-wax is an example of the latter class, and ice probably of the former.

In many cases there is an increase of volume as a body

passes from the solid to the liquid state, but in others, such as ice, there is a considerable diminution. In all cases a quantity of heat is rendered latent by the change. When the liquid state has been *completely* assumed any further increase of temperature will generally increase the volume of the liquid also. The coefficient of increase of volume is greater in liquids than in solids, and, just as in the case of solids, it is greater at a high temperature than at a low one.

If we continue to heat the liquid it will ultimately assume the gaseous state, and during the process of change a great quantity of heat will be rendered latent, and a very considerable expansion will under ordinary circumstances take place. There is some reason to think that, just as in the previous case so here, the state of a perfect gas is not instantaneously assumed, and that a vapour in contact with the liquid which produces it is not a perfect gas. If however this vapour, separated from the liquid, be allowed to expand in volume while its temperature is not diminished, it will approach more and more to the state of a perfect gas.

161. We shall afterwards see, when we come to treat of the conduction of heat, that the thermal conductivity of a body becomes lessened as its temperature increases: and, under the head of Specific Heat, we shall also find that this quality of a body becomes altered by change of temperature. In the meantime let us endeavour to shew how the other properties of a body are altered by increase of temperature.

EFFECT OF TEMPERATURE UPON THE REFRACTIVE AND DISPERSIVE POWERS OF SUBSTANCES.

162. One of the first experiments on this subject was that made by Jamin, who gradually cooled down water to

the freezing point, and found that as it cooled its index of refraction went on gradually increasing even after the point of maximum density (4°C) had been reached. This observation was afterwards confirmed by Messrs. Dale and Gladstone, who however found that the inversion at 4°C of the behaviour of water was not without influence on the refraction, and the following table exhibits the result of their inquiries regarding the refractive index of water at different temperatures.

Temperature of the water.	Refractive index for line <i>A</i> of the solar spectrum.	Refractive index for line <i>D</i> of the solar spectrum.	Refractive index for line <i>H</i> of the solar spectrum.
$^{\circ}\text{C}$		1.33374	
1	1.32913		1.34377
2	1.32913		1.34377
3	1.32913		
4	1.32902	1.33367	1.34366
6.5		1.33356	1.34366
9	1.32882	1.33342	1.34337
11	1.32879		1.34331

Messrs. Gladstone and Dale have since examined a great many different liquids: their mode of research being to use the liquid as a fluid prism by which to obtain a solar spectrum; and they have found—

1. *That the refraction uniformly diminishes as the temperature increases.*
2. *That the solar spectrum given by the substance diminishes in length; that is, the dispersion becomes less as the temperature increases.*

EFFECT OF TEMPERATURE UPON THE ELECTRICAL PROPERTIES OF BODIES.

163. Thermo-electric currents. It was discovered by Seebeck that if a circuit composed of two different metals

soldered together have one of its junctions heated, an electric current will be produced. Thus in Fig. 39, if the lower plate be made of bismuth and the sides and upper plate of copper, and if one of the junctions be heated, then a current of electricity will circulate in such a manner that there will be at the heated junction a flow of positive electricity from the bismuth through the copper to the cold junction. The direction of this current is represented by the arrow-head. The existence of this current may be easily rendered evident; for we have only to place the compound circuit with its length in the magnetic meridian, so that a magnetic needle inside will take the direction *CC*, and then by heating the junction *C* by means of a lamp the north pole of the needle will be deflected as in the figure. The current so produced is called a thermo-electric current.

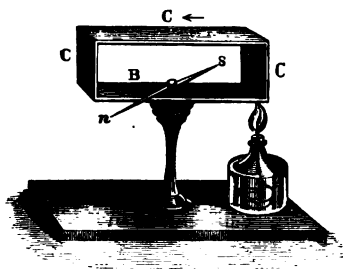


Fig. 39.

164. Thermo-electric series. If a compound circuit be made with any two metals in the following list, the positive current will go across the heated junction from the metal nearest the top to that nearest the bottom of the list:—

Bismuth	Tin	Silver	Antimony
Nickel	Copper	Zinc	Tellurium.
Lead	Platinum	Iron	

It will be seen that bismuth and antimony are nearly at opposite extremities of this table, and as both these metals are easily obtained they are generally employed in thermo-electric combinations.

165. Thermo-pile ; radiomicrometer. It was formerly assumed that the current produced by heating the junction of a compound circuit is proportional to the difference in temperature of the two junctions. It will be afterwards seen (Art. 166) that when the heating is very great this law does not hold, but if the junction be heated only slightly it will represent the truth. In this latter case, if we can find means to measure the strength of the current we obtain at the same time a measure of the difference in

temperature of the two junctions, and thus the combination will be equivalent to a differential thermometer.

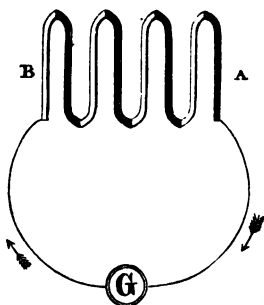


Fig. 40.

In adapting a thermo-electric arrangement to this purpose three things have to be borne in mind, if great delicacy be desired. In the first place, it will be necessary to produce as strong an electric current as possible ; in the second place, we ought to render this

current as effective as possible in deflecting a magnetic needle ; and in the third place, we ought to magnify the smallest motion of the needle so as to make it visible.

In order to produce as strong a current as possible, a number of pieces of antimony and bismuth are soldered together, as in Fig. 40, and when the heat is applied to the upper junctions we have the united effect of all the currents at the hot junctions passing through the circuit, including the galvanometer, in the direction of the arrow-heads.

In practice a square block, containing altogether twenty-five couples of bismuth and antimony, is generally employed, and such an arrangement is called a thermo-pile. This

instrument is however incomplete without a galvanometer; and we shall now shortly describe Lord Kelvin's reflecting galvanometer, which is admirably adapted for use with the thermo-pile. In this galvanometer a small magnet m (Fig. 41) acts as a magnetic needle; it is attached to the back of a small flat circular mirror which is delicately suspended by a fine thread. The needle is surrounded by coils of the wire which conveys the current of the thermo-pile, and when the current is passing, the needle and attached mirror will of course be deflected out of their previous position. But the needle m is under the influence of the earth's magnetism, and under ordinary circumstances a very weak current coming from the thermopile would be able to turn this needle only a very little distance out of the magnetic meridian before it would be stopped by the earth's magnetic force tending to bring it back. A rather large magnet M (Fig. 42) is however placed in such a position as to counteract as nearly as possible the earth's magnetic force upon the needle m which is inside G . The consequence of this arrangement will be that, whereas without M the earth's magnetic force would overcome the current when the magnet m had been deflected but a little way, now, the earth's magnetic force on m being very nearly counteracted by means of M , the magnet m will behave as if it were nearly astatic, and will describe, when acted on by the current, a very much larger arc before it is stopped.



Fig. 41.

In the next place, a small motion of m is rendered visible by the following means. Since the needle is attached to the back of a freely-suspended mirror, any motion of the needle will of course be followed by an angular deviation of the mirror. Now the light from an illuminated slit s ,

having first been made to pass through a small lens in the galvanometer *G*, falls upon the mirror and is reflected back in the line *Gs'* so as to throw an image of the luminous slit upon a graduated scale. It is evident from this arrangement that a comparatively small change in the plane of the mirror will produce a very large change in the position of the luminous image on the scale. Also, from what has

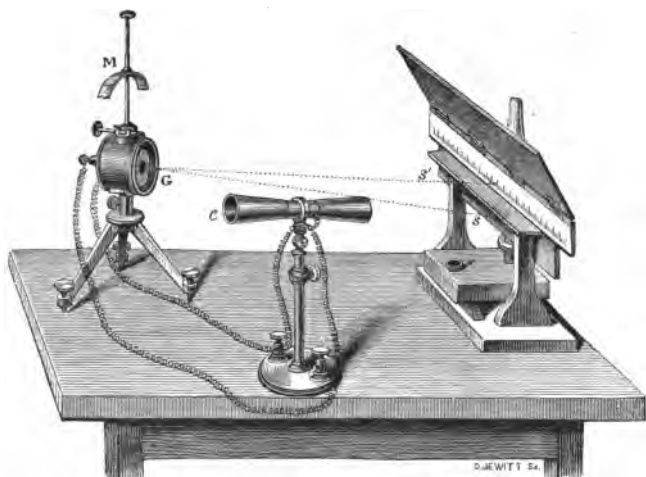


Fig. 42¹.

been said it will be seen that this instrument combined with the thermo-pile will have all the requisites of a very delicate differential thermometer. For, in the first place, by means of a pile with a number of pairs we produce a strong current of electricity; secondly, the needle is very sensitive to the influence of this current; and thirdly, small motions of the needle are magnified so as to be rendered

¹ This figure is here inserted by the kind permission of the late Mr. C. Becker of Messrs. Elliott Brothers, London.

easily visible, being at the same time strictly proportional to the strength of the current which causes them. When used to indicate the presence of radiant heat the pile is generally furnished with a brass cone *c*, the interior of which is polished; by which means not only the heat which directly reaches the pile itself but that which falls upon the cone is ultimately reflected upon the face of the pile, and its sensibility is thereby greatly increased. In the figure there are two brass cones, but in the experiment we are describing only one of these is exposed to the source of heat, the other being shut by a brass cover. The junctions of the pile are also usually covered with lamp-black, a substance which absorbs nearly every kind of radiant heat. So delicate may an arrangement of this description be made, that if a substance be presented before the cone *c* one degree Fahr. hotter than the pile itself, the *mere radiation* from this substance, by very slightly heating the one face of the pile, will in some instruments cause a change in the position of the reflected luminous image equal to 50 or 60 divisions of the scale.

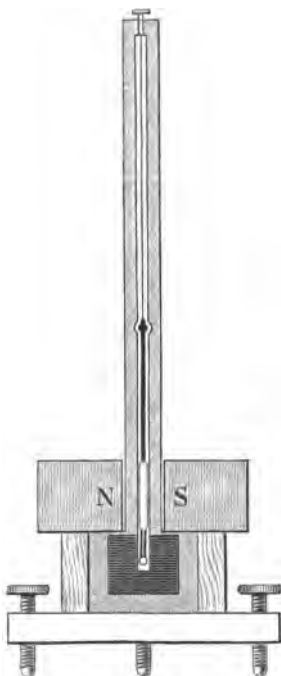


Fig. 42 a.

To Prof. Boys is due an exceedingly sensitive arrangement in which thermo-pile and galvanometer are combined in one instrument, called a *radiomicrometer* (Fig. 42 a). To the lower ends of a single loop, 1 inch long and $\frac{1}{16}$ inch

wide, of fine bare copper wire are soldered light bars, $\frac{1}{8}$ inch long, of antimony and bismuth whose other ends are soldered to a thin copper disc, $\frac{1}{16}$ inch in diameter, or to a narrow strip of thin copper foil. The loop is attached to the lower end of a very light glass tube, 2 inches long, which is suspended by a quartz fibre, 4 inches long, and the whole is hung in a thick brass tube with the loop between the pole-pieces of a strong permanent steel magnet.

When radiation is allowed to fall on the blackened face of the copper disc, the lower junction of the couple is heated and a current traverses the loop, which, being in a magnetic field, is turned about a vertical axis until the twisting moment due to the mutual action of the current and the field is balanced by the twist-resisting moment of the quartz fibre; and the amount of deflexion is indicated, as in the reflecting galvanometer, by means of a light mirror attached to the glass tube. The couple is screened from the action of the magnet by a thick iron casing, and the thick brass tubing prevents the interior from being unequally heated by casual external causes.

On account of its great delicacy an arrangement of this kind is eminently adapted to researches on radiant heat—as we shall see when we come to that branch of our subject.

166. Thermo-electric inversion. It was at first supposed that the current produced by heating one junction of a compound circuit would prove to be proportional to the difference in temperature between the two junctions. This, however, is not strictly the case. Cumming was the first to shew that in a circuit of certain metals, if one junction is kept cool while the other is gradually raised in temperature, the current, instead of going on regularly increasing, begins to diminish, then comes to a stop, and ultimately

sets in the opposite direction. This observer found that if gold, silver, copper, brass, or zinc wires be heated with iron the direction of the current becomes changed at a red heat. This subject has recently been investigated with much completeness by Professor Tait.

167. Pyro-electricity. Certain minerals when heated acquire electrical properties. One of these is tourmaline, in which this effect of heat was originally discovered by observing that when brought into contact with hot ashes it first attracted and then repelled them. It was found by Canton that it is not the absolute temperature but change of temperature which renders a tourmaline electric. Suppose, for instance, we have a tourmaline whose poles we call *A* and *B*. If this tourmaline be kept sufficiently long in a medium of constant temperature it will exhibit no electric manifestations. If it be transferred into a warmer medium, *A* will exhibit positive and *B* negative electricity; while if transferred into a colder medium, *A* will exhibit negative and *B* positive electricity.

A similar property is possessed by other crystals, and Haüy was the first to remark that those crystals are pyro-electric which are deficient in symmetry.

168. Effect of temperature upon the electric conductivity of bodies. Pure metals. This subject was first studied by Sir H. Davy, but a much more accurate research is that of Dr. A. Matthiessen and M. Von Bose, who have obtained the results given in the subjoined table.

We see by comparing together the first and third columns of this table that the proportion between the electric conductivity of the different metals is very nearly the same at 100°C as at 0° , while by the second column we see that the decrement between 0° and 100° is nearly 29 per cent. for each metal.

Electric Conductivity.

Name of Substance.	At 0°C.	100°C.	
	Silver at 0°C = 100.	Silver at 0°C = 100.	Silver at 100°C = 100.
Silver (hard drawn) .	100.00	71.56	100.00
Copper (hard drawn)	99.95	70.27	98.20
Gold (hard drawn) .	77.96	55.90	78.11
Zinc	29.02	20.67	28.89
Cadmium	23.72	16.77	23.44
Tin	12.36	8.67	12.12
Lead	8.32	5.86	8.18
Arsenic	4.76	3.33	4.65
Antimony	4.62	3.26	4.55
Bismuth	1.245	0.878	1.227

A later research by Dr. Matthiessen and C. Vogt shews that thallium and iron are exceptional in their behaviour, and that for thallium the decrement between 0° and 100°C is 31.42 per cent. In like manner the decrement for pure iron between the same limits was found to be 38.26 per cent.

168 a. Bolometer. The variation of the electric conductivity of metals with temperature was utilized by Professor Langley in 1881 in the construction of an exceedingly sensitive measurer of radiation.

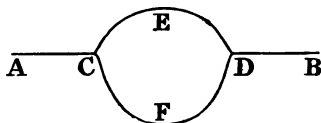


Fig. 42 b.

If an electric current is passed from *A* to *B* along a circuit *ACDB* which in the part from *C* to *D* is made up of two branches, *CED*, *CFD*, then to every point *E* in the one branch corresponds some one point *F* in the other such that if these points are directly connected by a wire no current passes through this wire; these points, in fact, divide the branches into parts whose resistances are in the same ratio. The variations of resistance of one of these

parts, *CE*, can thus be determined, and consequently its changes of temperature and the amounts of heat absorbed by it when submitted to radiation can be estimated.

In Professor Langley's instrument, by which a variation of $\frac{1}{100000}$ degree Cent. can be measured, each of the parts *CE*, *ED*, is made of a grating formed by stamping out of thin platinum foil a series of parallel strips, $\frac{1}{2}$ inch long and $\frac{1}{80}$ inch wide, so connected as to form a continuous circuit. This grating is placed at the bottom of a cylindrical ebonite box, about 5 inches deep and of $\frac{3}{4}$ inch internal diameter, which is lined with copper to secure uniform temperature in the interior and is furnished with several centrally perforated ebonite diaphragms to prevent air-currents while allowing radiation to pass: and wires are led through the thick ebonite base from the ends of the grating to binding screws on the outside of the box, by means of which the necessary electrical connexions are made. If electrical equilibrium is first established with both gratings shielded from radiation, and then one of them is exposed, the rise in temperature of the exposed grating due to the incident radiation can be determined from the change of adjustment necessary to restore equilibrium.

169. Liquids. Marianini was the first to shew that an increase of temperature exalts the electric conductivity of liquids, and his results have since been confirmed by Becquerel who made experiments on solutions of sulphate of copper and sulphate of zinc and on the nitric acid of commerce. From these it appears that a difference of from 20 to 30 degrees C suffices to double the conductivity of these liquids, probably by facilitating electrolysis.

170. Bad conductors. Heat converts many insulating solids into conductors by making them liquid, and of these a notable example is ice, which insulates when solid, but conducts electricity in the fluid state; also glass, resin, and

wax, which insulate at ordinary temperatures, become conductors at a temperature sufficient to soften them, and their conductivity is still more increased when they assume the liquid state. There are, nevertheless, many substances in which igneous fusion does not develop conducting power, and of these sulphur, phosphorus, and camphor may be quoted as examples.

Finally, the loss of electricity in dry air increases very sensibly with the temperature.

EFFECT OF TEMPERATURE ON MAGNETISM.

171. If we heat a magnetised bar of hard steel we produce a diminution in its magnetism, but if the heating be not too great, when again cold it will recover its former state. In such a magnet, therefore, the intensity will be a function of the temperature. But if this bar be brought to a white heat it will totally lose its magnetism, and will not recover it when again cooled.

Besides the reversible action above stated there is reason to think that all changes of temperature, whether from cold to hot or from hot to cold, diminish to some extent the permanent magnetism of a steel bar.

In like manner a soft iron bar when it is brought to a red heat is no longer attracted by a magnet. Nickel also ceases to be magnetic at the temperature of boiling oil, or about 600° Fahr., and cobalt at an extremely high temperature.

It is probable that change of temperature produces a complex change not only in the magnetic qualities of iron but also in its whole molecular structure.

Professor Barrett (working out an observation by Mr. G. Gore) finds that when an iron wire is just heated to whiteness and then allowed to cool, as it reaches a point of barely visible redness a sudden cherry-like glow takes place accom-

panied with a momentary elongation. This phaenomenon is known as *recalescence*.

Professor Tait likewise shews that iron exhibits an anomalous thermo-electric deportment at a red-heat, and suggests that iron becomes almost a different metal on being raised above a certain temperature.

EFFECT OF TEMPERATURE ON CHEMICAL AFFINITY.

172. An increase of temperature in a great many instances promotes chemical combination. Thus phosphorus, if slightly heated in oxygen or air, takes fire; and, generally speaking, a large number of bodies which do not combine together at ordinary temperatures do so when the temperature is increased.

Sometimes, however, heat promotes chemical decomposition, especially when the products of such decomposition are gaseous. Thus, if limestone be heated it parts with its carbonic acid gas and is converted into lime. Many substances, too, which possess little chemical stability, decompose on the application of heat, often with explosive violence. The terchloride of nitrogen, and the various fulminates, are examples of this class. The effect of heat upon the solvent powers of bodies has been already alluded to.

EFFECT OF TEMPERATURE ON OTHER PROPERTIES OF MATTER.

173. It is well known that an increase of temperature alters the behaviour of a liquid in a capillary tube. M. Wolf in 1857 and M. Drion in 1859 made some interesting experiments on this subject, in which the capillary tubes containing the liquids were heated very considerably under pressure. M. Drion has come to the following conclusions:—

1. That for the liquids studied the capillary meniscus

remains concave until the moment of complete evaporation ; its form at that instant being plane.

2. That for the same liquids the capillary ascension and curvature diminish as the temperature rises, until the moment of complete conversion of the liquid into vapour.

An increase of temperature affects also the extensibility of bodies. Wertheim has made numerous experiments on this subject, and he finds that in general metallic threads offer more resistance at a low than at a high temperature to a force tending to elongate them, so that the proportional elongation produced by a given weight is smaller in the first case than in the second.

To this law, however, iron and steel present an exception, their resistance to elongation augmenting from -15° to $+100^{\circ}\text{C}$, while at 200° it is not only smaller than at 100°C but sometimes even smaller than at ordinary temperatures.

In like manner the tenacity of a metallic wire, as estimated by its breaking stress, is altered by increase of temperature. This subject has been studied by Wertheim and also by Baudrimont, by whose researches it appears that the effect of heat is to some extent irregular, tending sometimes to diminish and sometimes to increase the tenacity if one does not go above 200°C . At a red heat, however, the tenacity of iron is very much diminished.

According to the experiments of M. Grassi the compressibility of water under pressure diminishes as the temperature increases, while heat, on the contrary, appears to augment the compressibility of ether, alcohol, and chloroform.

In like manner the cohesion and the hardness of bodies are diminished by heat, their crystalline form is altered, and indeed there is no property of matter that is not affected by this agent, although it is only in a few cases that its effects have been accurately examined.

BOOK II

ON THE LAWS WHICH REGULATE THE DISTRIBUTION OF HEAT THROUGH SPACE



CHAPTER I.

Radiant Heat. (Preliminary.)

174. It has already been stated on a previous occasion (Art. 5) that a body parts with its heat in two ways, namely,—

1. By contact with a cold body,
2. By radiation through space ;

and in order to render this distinction very evident it is only necessary to mention a familiar instance of each method.

When one end of a poker is heated in the fire the heat is gradually conveyed to the other end through the substance of the poker. This is an instance of communication of heat by contact, the cold particles receiving heat from the warmer ones next them, and in their turn conveying it away to still colder particles, until *after the lapse of a considerable time* it reaches the other extremity of the poker.

Now in this case it is evident that the particles at the cold end are not *immediately and directly heated* by those at the hot end, but only through the agency of the intervening

particles, and the great characteristic of this process is its exceeding slowness. It is very clear that this cannot be the method by which we receive heat from the sun, and indeed we have no reason to think that there is matter capable of retaining heat between the earth and our luminary. The effect in this instance is certainly not due to the heating of the intervening regions, but, on the contrary, it is as powerful in a very cold atmosphere as in a warm one, and may even be felt behind a screen of ice. We know, too, that light, and probably also heat, reach us from the fixed stars, although these bodies are vastly more distant than the sun.

It is this heating emanation which we term radiant heat, and in its character and distribution it is subject to certain laws, which we shall now proceed to describe. In the first place—

175. Radiation of heat takes place in vacuo as well as in air. For it takes place between the sun and the earth and between the fixed stars and the earth, and we have no reason to think that all space is filled with some kind of air.

176. Radiation takes place equally on all sides. If a sphere be heated and very delicate thermometers be placed on different sides of such a sphere at equal distances from the centre, they will always give the same indications. Such a sphere will also appear equally luminous from all sides.

177. Radiant heat traverses void space in straight lines and with the same velocity as light, that is to say, at the rate of about 186,000 miles in a second. The best proof of this statement is derived from the great probability, if not certainty, that heat and light are varieties of the same physical agent. This subject will be considered at a subsequent part of this book.

178. Radiant heat is capable of passing through certain substances without sensibly heating them. If a plate of rock salt be placed between us and the sun, we shall yet feel to a very great extent the effect of his beams; few of his rays will be stopped, and the screen will not be heated to a perceptible extent.

We may therefore infer that radiant heat passes through certain substances without being perceptibly absorbed or heating them to a sensible extent.

It is, however, probable that no substance is perfectly transparent with respect to heat (or diathermanous, as it is termed), and that all bodies are heated to a greater or less extent by the passage through them of calorific rays.

179. Radiant heat is probably not a substance emitted by a hot body, but an undulatory motion conveyed through a medium which pervades all space. Apart from the difficulty of conceiving space to be traversed by excessively minute particles all moving with the uniform velocity of 186,000 miles per second, the undulatory theory has furnished abundant evidence that light is due to a progressive wave-like motion in a medium pervading space, and much of this evidence applies likewise to radiant heat. This hypothesis is now very generally received.

It will be convenient here to define the various terms connected with undulatory motion. If a stone be dropped into a pool of water, a series of waves consisting of crests and hollows succeeding one another will spread outwards from the centre of disturbance. Now the distance between two contiguous crests or between two contiguous hollows is termed the *wave length*, because in this distance is embraced the whole variety of motions which together constitute a wave. When the ocean is agitated by a storm we have also waves, but here the wave length is obviously much greater than in the case above mentioned. We thus see that the

same substance may be the medium of propagating waves of different lengths. In these instances the direction of disturbance is up and down, while the direction of propagation is horizontal; and thus the displacement of a particle is in a direction at right angles to that of transmission of the wave.

In air we have another substance capable of conveying undulations of different wave lengths. These undulations constitute musical sounds, the *wave length* defining the *pitch* of the note. Thus if one note be an octave lower than another, its wave length will be double that of the other. The waves of sound are, however, different from those of water, inasmuch as they are not waves made up of crests and hollows, but of condensations and rarefactions succeeding one another; the direction of displacement of the air, instead of being at right angles to that of transmission of the wave, being in the same direction. We have thus two varieties of waves—

1. Waves of crests and hollows, where the direction of displacement is perpendicular to that of transmission.
2. Waves of condensation and rarefaction, in which the direction of displacement coincides with that of transmission.

Now whether light and heat rays consist of undulations of the first or of the second description, in either case we are entitled to expect that difference of wave length will denote some important difference in the quality of the ray. There are many considerations which induce us to imagine that difference of *colour* is denoted by difference of *wave length*, and that red, orange, yellow, green, blue, indigo, and violet have all their peculiar wave lengths. There are other considerations which induce us to imagine that these wave lengths are very small, being for violet rays no longer than $\cdot 0000167$, and for red rays $\cdot 0000266$ of an inch, while for

heat rays we shall afterwards see that the wave length is somewhat longer than for red rays.

But again, there are strong reasons for believing that waves of light consist of crests and hollows, while sound waves consist of condensations and rarefactions. There is this important distinction between the two cases. If we hold a string somewhat tightly in a horizontal direction and strike it from above downwards, we perceive speeding along it a crest and hollow wave for which the direction of displacement is in a vertical plane. And if we strike it from the side we perceive a similar wave, for which the direction of displacement is in a horizontal plane. We can have thus two sets of crest and hollow waves proceeding in the same direction along the string, the plane of vibration of the first being at right angles to that of the second; but it is evident that we can have no such distinction in waves of condensation and rarefaction. Now when the vibrations of a crest and hollow wave are always confined to the same plane, that wave is said to be *polarized*. Thus in such a wave proceeding in a horizontal direction, if the vibrations of the particles be confined to a vertical plane, the wave is polarized; and if they be confined to a horizontal plane it is also polarized, but in a direction at right angles to the former: but if these vibrations have no reference to any particular plane then the wave is unpolarized.

Now there are certain processes by which a ray of ordinary light may be broken up into two rays that appear to have reference to planes at right angles to one another. By such a process the ray is said to be polarized. And this fact entitles us to assume that waves of light are crest and hollow waves and not waves of condensation and rarefaction, since these last from their nature cannot have a reference to any particular plane.

180. The amount of radiation falling on a given

area varies inversely as the square of the distance of the area from the radiating body. It would appear that this law ought theoretically to hold good whether we consider radiant heat to be particles ejected by a heated body, or to be an undulatory movement of an ethereal medium proceeding outwards from the body. In either case the amount of *vis viva* which at one moment, and at the distance (say) of one mile from the centre, covers the surface of a sphere of which the radius is one mile, will at another moment and at the distance of two miles from the centre cover the surface of a sphere of which the radius is two miles; that is to say, the same amount of *vis viva* or *heat* will have spread itself over a surface four times as large, and hence the amount of *vis viva* or *heat* which falls upon unit of area, or in other words the intensity, will be diminished four times, and will therefore vary inversely as the square of the distance.

The following ingenious experimental verification of this law was first given by Melloni. Suppose that we have a large red-hot wall before us and that we view it through a small tube, blackened in the inside, held close to the eye. The opening of this tube farthest from the eye will appear to be red hot, and it will appear equally so whether we approach the eye and tube close to the wall or withdraw them to a distance, always *provided that the wall be large enough to fill up the field of view from the eye*. If the eye and tube be far from the wall, we embrace in the field of view a much larger extent of the wall, but we view it from a greater distance, and it thus appears that what is gained in extent is lost in distance, seeing that in this case the same amount of light reaches the eye at all distances. Now we know that the *extent* of heated surface viewed in this manner varies *directly as the square of the distance*, therefore we see that *the heat which reaches the eye from*

a given extent of surface must vary inversely as the square of the distance.

Melloni applied a tube of this kind not to the eye but to a thermo-pile (which is very sensitive to heat rays, just as the eye is to those of light), and he found that the indication of the galvanometer, and hence the amount of heat acquired by the pile, was the same whether the pile was near the hot wall or far from it, provided always that the wall was sufficiently large to fill up the field of view from the pile.

CHAPTER II.

Reflexion, Refraction, &c. of Radiant Heat.

181. The laws of radiation which have been stated in the preceding chapter are sufficient to exhibit the great similarity between radiant light and heat, and even to render it probable that both these effects are due to the same physical agent.

Our belief in this is greatly strengthened by observing that the various phaenomena of optics are reproduced in radiant heat, and it is to a consideration of these analogous properties that the present chapter will be devoted. We shall mainly direct attention to the following properties of radiant heat—

1. Reflexion.
2. Refraction.
3. Absorption.
4. Polarization and double refraction.

But, in the first place, we shall make a few preliminary remarks on the spectra of heated bodies.

182. Newton was the first to prove that a ray of sun-

light really contains, blended together, a very great number of simple rays, each exhibiting a different colour; and his fundamental experiment may be shortly described as follows.

Let us take a glass prism, and place it with its edge vertical, and let a horizontal ray of sunlight strike obliquely against its side. As this ray passes through the prism it will be bent in such a manner that its line of exit will differ very much in direction from that of incidence. But, besides this, each simple coloured ray of which the compound ray is composed will be bent by the prism in a different manner, so that the rays which entered the prism in the same direction will leave it in different directions, and we shall thus obtain in a separated condition all those variously coloured rays which together form a beam of white light. It is easy now to see what is meant by the term 'Spectrum.' Suppose, for instance, that by an arrangement similar to the ordinary photographic camera we were to throw upon a screen the image of a vertical line of light. Under ordinary circumstances this image would be a vertical *line*, but if a prism were interposed in the path of the rays each constituent of the light from the slit would be bent by it in a different direction, and we should have the vertical image of the slit due to one of these constituent rays thrown upon one part of the screen, and that due to another constituent ray thrown upon another part, and so on. We should thus obtain not *one* image of the slit *but a very great number of images* contiguous to one another, so as to form an oblong space illuminated by various colours. This space is called the spectrum of the line of light, and if the light be that of the sun, it is called the solar spectrum.

183. This oblong space, as we have observed, is differently coloured throughout. The following diagram

(Fig. 43), in which the left side represents the least and the right the most refrangible rays, will give an idea of the colour and comparative luminosity of the different parts of the solar spectrum. The ordinates of the curve denote the luminosity for each part, and it will be seen that the greatest intensity of light is in the yellow.

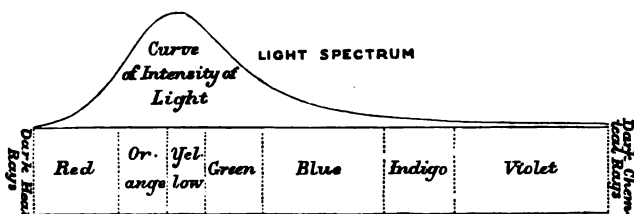


Fig. 43.

If now we obtain the solar spectrum by means of a prism, or set of prisms, which we are sure do not absorb any of the rays, or do so only to a very small extent, (and for this purpose we must use rock salt,) and if we estimate the heating effect of each portion of the spectrum by means of a thermopile, we shall from Sir W. Herschel's observations expect to find the curious result, which is roughly sketched in Figure 44, in which it will be seen that the

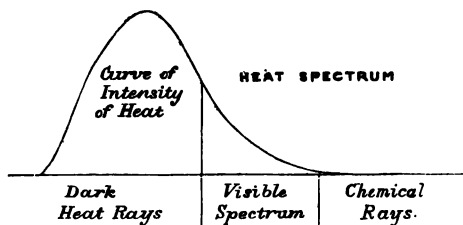


Fig. 44.

maximum heating effect is a good deal beyond the red, and that the rays which produce it are invisible to the eye.

If our instrument for measuring heat be delicate enough, we shall also find that the heating effect extends to the right as well as to the left of the visible spectrum, although in the former direction it is extremely feeble.

The foregoing conclusion of Sir W. Herschel has, however, been contested by Professor Langley, whose experiments with his exceedingly sensitive instrument, the bolometer, appear to shew that the maximum heating effect occurs in the neighbourhood of the yellow part of the visible spectrum (as for light), and that the joint effect of the infra-red and ultra-violet radiation is not so great as that of the visible part of the spectrum.

Besides the illuminating and heating powers of rays they have a third property, namely that of producing chemical action. Chloride of silver, it is well known, becomes blackened under the influence of light, and it is by making use of this property that we are enabled to obtain photographic pictures of bodies.

But the action of certain rays upon chloride of silver is much more energetic than that of others; this being most intense for the violet, or more refrangible rays, and even extending much beyond the visible extremity of the spectrum towards the right.

It has furthermore been recently shewn by Professor Tyndall that light decomposes certain vapours, such as nitrite of amyl, iodide of allyl, and some others.

Until very lately the tendency has been to believe that it is only the more refrangible rays that have the power of producing chemical effect. Captain Abney has however recently shewn that by employing a certain sensitive surface it is possible to photograph any kind of ray, and he can obtain by such means a picture of the solar spectrum shewing all the absorption lines that exist therein far beyond the visible spectrum on either side.

184. If we next proceed to consider the spectra of other luminous solid bodies, we shall find that these are very analogous to that of the sun, except in respect of certain dark lines, which we may for the present dismiss from our consideration.

If the temperature of the source be high, we have, besides a great deal of dark heat, a good amount of luminosity; but as the temperature decreases we perceive a very considerable diminution in the amount of light, until below a red heat the light has entirely disappeared and the whole of the radiation consists of dark heat.

Thus if the temperature of the source be low, the whole radiation is of the nature of that portion of the solar spectrum which lies in the diagram to the left of red. We shall afterwards see what experimental grounds we have for this assertion.

185. Dismissing in the meantime the chemical effect of rays from our consideration we may separate radiant heat into two kinds, the first embracing those rays which by means of the prism can be separated from light and which lie to the left of the visible rays in the spectrum, while the second denotes that heating effect which accompanies light and which cannot be separated from it by prismatic analysis. With regard to these we must now answer the two following questions:—

1. Is the dark heat beyond the red composed of rays similar in physical constitution to those of light?

2. In the portion of the spectrum which is visible, is the heating effect produced by the very same rays which produce the luminous effect, or are there two sets, the one heating and the other luminous, mixed together?

We shall best answer these questions by proceeding at once to state the various properties of radiant heat which have been experimentally proved, and then using these as

a means of comparing together the two agents heat and light.

REFLEXION OF HEAT.

186. Dark heat is capable of reflexion. The following experiment will exhibit the reflexion of heat.

Suppose that we have two concave metallic reflectors facing one another (as in Fig. 45), and let *A* be the focus

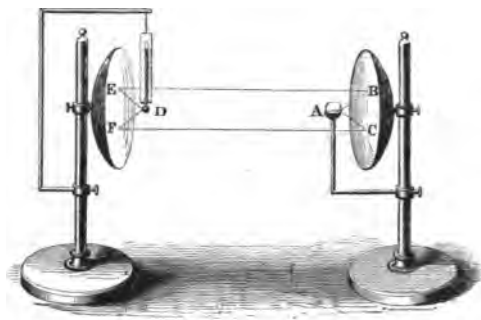


Fig. 45.

of the one and *D* that of the other. Let an iron ball, heated to a temperature somewhat below redness, be placed at *A*; if we place a piece of phosphorus at *D* it will probably take fire, or if we place a thermometer there its temperature will rise much more than if we placed it in any other position in the neighbourhood. The reason is, that the rays which leave the ball *A*, such as *AB*, *AC*, are reflected at *B* and *C* from the polished metallic surface of the one mirror in parallel lines *BE*, *CF*, while at *E* and *F* these are again reflected by the other mirror in the directions *ED*, *FD*, and thus converge upon the point *D*, the focus of that mirror.

In the heating of the thermometer placed at *D* we have

thus a proof of the reflexion of dark heat from a metallic surface.

Leslie has made numerous experiments with regard to the reflecting powers of bodies for dark heat. The following was the arrangement which he adopted at a time when the thermo-pile was yet unknown. In Fig. 46, m is a concave metallic mirror, and the source of heat is a cube containing hot water, the rays of heat proceeding from which would, if left to themselves, converge to a focus

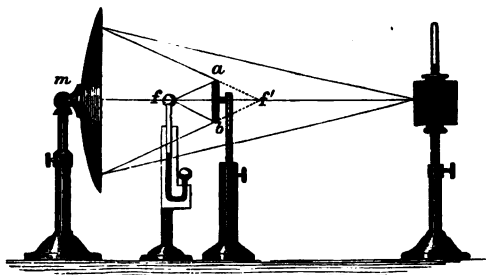


Fig. 46.

at f' ; but in consequence of a reflecting plate ab being placed in their path their focus is at f . It is clear that if the plate ab be taken away and another plate substituted in its place which reflects only half as many of the rays which fall upon it, then the heating effect at f will be reduced to one-half of its previous amount; in fact, this heating effect will be proportional to the reflecting power of the surface ab . Leslie measured this effect by means of his differential thermometer, an instrument which we have already described (Art. 29). By this means he obtained not the absolute reflecting power of any body or the number of rays which it reflects out of every hundred which fall upon it, but only the comparative reflecting

power of different surfaces. Calling that of brass 100, he obtained by these means the following result—

Brass	100	Lead.....	60
Silver	90	Amalgamated tin	10
Tin	80	Glass.....	10
Steel	70	Lamp-black.....	0

It will be seen from this list that metals which reflect light most copiously are also the best reflectors of obscure heat.

187. The heat which belongs to light is reflected in the same manner as the light. M. Jamin has shewn that if we take certain elementary rays, or, which is the same thing, a certain small portion of the spectrum, the reflecting power of any substance with respect to the light of this portion will be as nearly as possible the same as its reflecting power for the heat. We thus obtain the following table, in which any small difference between heat and light may be attributed to error of experiment.

Metal used for reflecting.	Green of the Spectrum.		Red of the Spectrum.	
	Reflecting power for heat. light.		Reflecting power for heat. light.	
Platinum	59	—	60	—
Zinc	65	62	60	58
Metal of mirrors . .	58	62	65	69
Brass.	63	62	75	72

188. Variation of the reflecting power with the angle of incidence. It has been proved by MM. de la Provostaye and Desains that the reflecting power of glass for heat increases very rapidly with the angle of incidence, and that the law which regulates this augmentation is, as

nearly as we can perceive, the same as that which holds for light.

These observers have also found that the reflecting power of metallic surfaces for heat varies very slowly with the incident angle, a peculiarity which metals also possess with regard to light.

189. Diffuse reflexion of heat. MM. Provostaye and Desains, and also Knoblauch, have made experiments on this subject, and they find that as in the case of light some of the rays are scattered about by the surface and reflected in an irregular manner, so also with regard to heat there is a diffuse reflexion or scattering about of the rays. The laws of this are not exactly known, but what is known tends to strengthen the argument in favour of the identity of light and heat.

190. As the result of the experimental researches made with regard to the reflexion of heat, we find:—

1. Dark heat in the same manner as light is reflected very copiously by metals.

2. Heat, whether reflected from a surface of glass or from one of metal, is subject to laws precisely similar to those of light, whereby the intensity of the reflected beam is connected with the angle of incidence.

3. Heat, in the same manner as light, suffers a scattering or diffuse reflexion from the surface of bodies.

4. If we confine our experiments to a part only of the spectrum, we find that the light of this portion is reflected by a surface precisely in the same manner as the heat.

We are therefore disposed to conclude that, *as far as reflexion is concerned, dark heat is subject to the same laws as light, and also that, if we take any region of the visible spectrum, its illuminating and heating effects are caused by precisely the same rays.*

REFRACTION OF HEAT.

191. When Sir W. Herschel first noticed that there was a heating effect beyond the red of the visible solar spectrum, this observation implied the refraction of heat. But Melloni was the first to prove experimentally that the heat which emanates from a non-luminous source is capable of refraction. His success in these experiments was due to two very important aids.

In the first place, he found that a plate of rock salt allows almost every sort of dark heat to pass through it readily, while every other substance powerfully absorbs this kind of heat.

By using a rock-salt prism he was thus sure that the heat would not be stopped by the substance of his prism. Furthermore, Nobili and Melloni were the first to employ

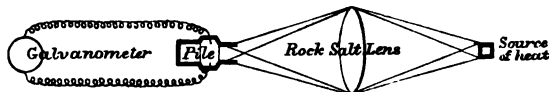


Fig. 47.

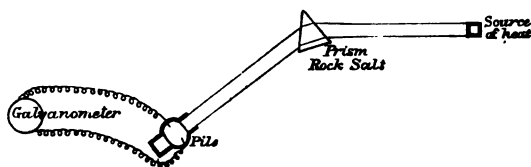


Fig. 48.

the thermo-pile for investigations of this nature, and by an improved arrangement of this instrument the latter was enabled to detect the presence of an exceedingly small amount of radiant heat. (This instrument has been already

described, Art. 165.) By means of these two important experimental adjuncts Melloni was able to render manifest the concentration of dark heat upon the focus of a rock-salt lens, and also to shew that it is bent by a rock-salt prism; thus proving conclusively the refrangibility of such heat. The method of experiment is illustrated in Figs. 47 and 48. The subject was afterwards taken up by Forbes, who shewed that the refrangibility of dark heat is inferior to that of the luminous rays. By a method founded on the total reflexion of heat he obtained the following indices of refraction, the substance being rock salt.

Indices of refraction.

Mean luminous rays	1.602
Heat from Locatelli lamp	1.571
Heat from incandescent platinum	1.572
Heat from brass at 700° Fahr.	1.568

It is important to compare this result with that obtained by Sir W. Herschel, who found dark rays beyond the red of the visible spectrum, and consequently found that they were less refracted than light rays. We thus see that dark rays of a less refrangibility than light belong alike to sources of heat of low temperature, and to those of high temperature, such as the sun; the difference being, as we have already remarked, that bodies of low temperature give out only dark rays, whereas those of high temperature give out also luminous rays. Pursuing his researches on this subject, Forbes found that the wave length of the heat rays was most probably considerably greater than that of the light rays, a result in accordance with the optical determinations of Fraunhofer and others, who have found the wave length of the red rays greater than that of the more refrangible rays of the spectrum. We thus see that *both as regards refrangibility and wave length the dark spectrum appears to be the appropriate prolongation of the luminous one.*

ABSORPTION OF HEAT.

192. The discovery by Melloni, that rock salt is a body which transmits heat freely, sufficiently indicates that most substances which are transparent for light are not so with regard to heat. In the language adopted by scientific men this is expressed by saying that most substances are *athermanous*, and that rock salt is almost the only *diathermanous*¹ substance, easily procurable in a state convenient for experiment, the two words italicised corresponding to the terms *opaque* and *transparent* in the science of optics. There are two facts regarding the absorption of heat that may with advantage be discussed here. In the first place, *when the heat which radiates from a hot body has passed through one screen it is more easily able to penetrate another screen of the same material.* This was originally observed by De la Roche, and his observations have since been abundantly confirmed by Melloni, Forbes, and others. They have expressed it as a sifting of the radiant heat by its passage through the first screen; certain rays being stopped and only those allowed to proceed which are of a nature easily able to penetrate the material of the screen. It will be observed that this is quite analogous to the action of a red screen upon light, which stops the blue rays but allows the red to pass, nor will these red rays be much diminished by a second screen of the same material.

A selective absorption both for heat and light is thus exercised by solid and liquid bodies, in virtue of which certain rays are set apart to be stopped while certain others are allowed to proceed.

It may be remarked that besides *selective* absorption of

¹ Dr. Schultz-Sellack (Phil. Mag., May 1870) considers it probable from his experiments that the haloid compounds of all elements in a solid or liquid state are partially diathermanous for lamp-black heat at 100°C: likewise many sulphides.

rays by substances there is probably also a more *general* absorption, which may conveniently be kept separate from the former. We have some grounds for believing that very thick strata of air, water, glass, or any substance seemingly transparent, will ultimately stop light, possibly at a rate not greatly differing for the different rays.

But to return to *selective* absorption. We have reason to think that this property, as regards both light and heat, is strongly marked in gases: indeed the vapour of sodium is found to be quite transparent for every kind of light except for that from a salt flame, for which it is quite opaque, and Professor Tyndall has also observed a similar action of gases with respect to radiant heat.

We remark, in the second place, *that most substances, including those that are transparent for light, are generally opaque for dark heat of great wave length and small refrangibility.* Rock salt has been mentioned as an exception, but even this is not perfectly diathermanous. Provostaye and Forbes have both found that it passes a smaller proportion of heat rays than of light rays, and the author of this work has attempted to shew that the rays which it stops are those of very great wave length. Forbes has also shewn that transmission in general raises the index of refraction of the transmitted heat; in other words, a screen stops in preference those rays which have the lowest index of refraction or greatest wave length. But this rule, though very general, is not universal; for it has been found by Melloni and Forbes that smoked rock salt, and mica split by heat into a bundle of thin pellicles, transmit in preference dark rays; and by Tyndall that a solution of iodine in bisulphide of carbon has the property of completely stopping the light rays, while it allows dark heat to pass in great quantity. Tyndall found that a fluid lens formed of this solution and enclosed in rock salt will

stop all the light from an electric lamp, but permit the dark rays to pass in sufficient abundance to produce incandescence. We shall on a future occasion return to the important subject of absorption of heat.

POLARIZATION OF HEAT.

193. We have seen that there are analogies between light and heat as regards reflexion, refraction, and absorption; and it might be expected that the same should hold as regards polarization. Malus and Berard were the first to shew that the heat accompanying solar light is capable of polarization. In 1834 Professor Forbes took up the inquiry; but before describing his experiments it may be well to describe the action of tourmaline and glass with respect to light. If a plate of tourmaline be cut with its plane surface parallel to the axis of the crystal, and if a ray of ordinary unpolarized light be allowed to fall upon it, it divides the ray into two parts, one polarized in the plane of the axis, and the other in a plane perpendicular to the axis, and the former of these is absorbed while the latter is allowed to pass. The light transmitted through such a plate will therefore be polarized in a plane perpendicular to the axis of the crystal. If now a similar plate of tourmaline be placed behind the first, but with its axis at right angles to the axis of the first, then the light transmitted by the first will be absorbed by the second, so that the combination will be virtually opaque; if, however, we turn the second plate round until the axes of both plates coincide, then the combination will be transparent. Again, if a bundle of plates of glass or any similar substance, such as mica, be held together, and if a ray of light be allowed to strike obliquely at a certain angle upon it, part of this will be reflected and part will be transmitted through the plates. Now it is found that the reflected light is very nearly

polarized in one plane, and the transmitted light in a plane perpendicular to that of the reflected light ; and furthermore, if the reflected or the transmitted ray be again reflected or transmitted by a similar bundle of plates, but with its plane of incidence perpendicular to that of the first bundle, then the rays that have been reflected by the first bundle will not be reflected by the second, nor will those that have been transmitted by the first bundle be transmitted by the second. But if the plates are parallel, so that the planes of incidence coincide, then they will reflect or transmit the rays.

Now if radiant heat be similar to light, we should expect phenomena similar to the above ; and accordingly Forbes, by using two plates of tourmaline cut with their planes parallel to the axis, proved that there was a marked additional stoppage of heat (just as there is of light) when the axes of the two plates were crossed, whether the source of heat were a lamp or brass heated below luminosity. He also proved that heat, like light, is polarized in the processes of reflexion and refraction. In his refraction experiments he employed mica split by heat, and therefore acting like a bundle of plates. In this state the substance ordinarily transparent, assumes a glossy silvery appearance, and, though nearly opaque to light, allows nevertheless a large portion of heat to pass ; and if the rays of heat make a proper angle with the surface they are found to be polarized to a considerable extent, and hence two such screens placed in opposite directions are found to stop a large portion of the incident heat. This result was found to hold for all kinds of heat, including that from the blackened surface of a vessel containing boiling water. In addition to these results Forbes was able to prove the circular polarization and depolarization of heat. Circular polarization was proved by using a rhomb of rock salt, while by inter-

posing a film of mica between his polarizing and analysing plates, which had their planes of incidence inclined at right angles to one another, and observing whether any difference of heating effect appeared when the principal section of the plate was parallel to the plane of primitive polarization or inclined 45° to it, he shewed the depolarization of heat.

Other observers have confirmed these results and have furthermore shewn that *very many of the phenomena of optics can be reproduced by dark heat. Indeed, the analogy between these two agents is as complete as our experiments are capable of shewing.* Our instruments are doubtless very delicate, but it ought to be borne in mind that the most refined apparatus is far less sensitive for dark heat than the eye is for light.

CONCLUDING REMARKS.

194. The facts detailed in this chapter all tend to shew that radiant light and heat are only varieties of the same physical agent, and also that when once the spectrum of a luminous object has been obtained, the separation of the different rays from one another is physically complete; so that if we take any region of the visible spectrum, its illuminating and heating effect are caused by precisely the same rays. We may extend this observation to that region of the spectrum near the violet, or most refrangible extremity, which possesses not only a luminous but also a well known chemical effect, and assert that these two effects are caused by the same rays. The solar spectrum, it is well known, is intersected with dark lines, of which more hereafter; in the meantime suffice it to say that these lines have done good service in shewing that there is only one agent at one part of the spectrum. Thus towards the left extremity, or the red, we have at the same time a heating and a luminous

effect. Now whenever a dark line occurs this of course denotes that a certain ray of light is absent, but by means of very delicate investigations with the thermo-pile it has been found that heat as well as light is absent from the spaces occupied by these lines. Finally Captain Abney by a peculiar photographic process has shewed that chemical effect as well as light and heat is absent from these spaces.

So also towards the right extremity, or violet, we have at the same time a luminous and well known chemical effect, and we may therefore obtain a map of this region either from eye observations or by means of photography. Now when two maps obtained by these two different methods are compared together, it is found that the same dark lines occur in both, or, in other words, an absence of luminosity implies at the same time an absence of chemical effect.

Furthermore, we have reason to suppose that the physical distinction between different parts of the spectrum is one of wave length, and that rays of great wave length are in general less refracted than those of small wave length.

We would remark, in conclusion, that while the effects produced by different rays are generally divided into their heating, luminous, and chemical effects, yet there is a material distinction between the first of these and the other two. The luminous effect depends upon the constitution of the eye, and may be possessed by certain rays and by these alone; the chemical effect also, as it depends upon the nature of the substance and of the change which it undergoes, may be possessed by certain rays but not by others. But we are led to think that the heating effect of a ray is the true physical measure of its power, so that by making (as we can approximately make) any portion of the

spectrum wholly available in heating a body and by estimating exactly the heating effect which is produced, we shall at once know the amount of energy or *vis viva* of which this portion of the spectrum is possessed.

CHAPTER III.

Theory of Exchanges.

195. At an early stage in the history of radiant heat the following question arose. A hot body, we all know, radiates heat towards those bodies that are of a lower temperature than itself, but does it also radiate when surrounded by bodies of a temperature equal to its own or of a higher temperature? in other words, is the radiation of a given body at a given temperature dependent upon the bodies that surround it, or is it independent of these?

Either hypothesis will serve to explain the fact that bodies of the same temperature neither gain nor lose heat by virtue of each other's presence, for we may either suppose that such bodies do not radiate at all to one another, or else that each one radiates and receives back as much heat as it gives out. About a century ago Professor Pierre Prevost, of Geneva, introduced this latter idea, and ever since that time it has been gaining ground, and is now very generally received.

Prevost's theory was called by its author that of a *moveable equilibrium of temperature*, and according to it bodies at all temperatures are constantly radiating heat to one another, while those of a constant temperature get back as much heat as they give out. The equilibrium suggested by Prevost is not therefore a statical or tensional

equilibrium or one of repose, but it is essentially an equilibrium of action ; and viewed in this light it would seem to flow naturally from the dynamical hypothesis which views all heat as a kind of motion.

Let us take, for instance, a thermometer : this, according to the theory of exchanges, is constantly giving out heat at a rate depending on the temperature of the bulb and independent of that of the surrounding enclosure. On the other hand, it is receiving heat from this enclosure at a rate depending upon the temperature of the enclosure and independent of that of the bulb. Thus its heat-expenditure depends upon its own temperature, its heat-receipts upon that of the enclosure, and there is equilibrium of temperature when its expenditure is exactly balanced by its receipts.

196. A curious experiment by Pictet was probably the means of leading Prevost to this theory. Pictet, reversing the experiment of Art. 186 (Fig. 45), put ice, or a freezing mixture, in the focus of one of the reflectors, and a thermometer in that of the other. And in consequence of this the temperature of the thermometer was found to fall. This fall would be at once explained if we could suppose cold to be a principle susceptible of radiation. It was probably his conviction of the inadmissibility of this explanation that led Prevost to frame the theory of exchanges, and a very little consideration will shew that Pictet's phenomenon can be easily explained by this theory. Referring to Fig. 45, let us first take the case in which the bulb of the thermometer at *D* is of the same temperature as the substance at *A*. According to the theory of exchanges, rays *DE*, *DF*, &c. will proceed from the bulb *D*, and ultimately, by virtue of the laws of reflexion, will be concentrated upon the substance at *A*. In order therefore that the bulb *D* may not lose heat, it is necessary that the place of these rays

be supplied by other rays of equal intensity, that is, by *AB*, *AC*, &c. which proceed from *A* and ultimately fall upon *D*.

It thus appears that when *D* and *A* are of the same temperature both sets of rays are of equal intensity, and hence the thermometer will remain stationary.

Again, when *A* is warmer than *D* the rays which reach *D* from *A* are more intense than those which reach *A* from *D*, and hence *D* will gain heat, or the thermometer will rise; this is the ordinary experiment.

But, on the other hand, when *A* is colder than *D* the rays which leave *D* for *A* will be more intense than those which reach *D* from *A*, and hence *D* will be deprived of heat, or the thermometer will fall; this is Pictet's experiment.

We see therefore that the theory of a moveable equilibrium explains very well the apparent reflexion of cold, and that, according to this theory, the same cause which in the one case makes the thermometer peculiarly sensitive to an increase in the temperature of the opposite body (that is to say, the reflexion from the concave mirrors) will in the other make it equally sensitive to a diminution of the same temperature.

197. Besides this happy explanation the hypothesis of Prevost has consistently vindicated its claims to represent the truth, not only by explaining very many experiments, but also by suggesting new truths which have afterwards received an experimental verification.

This theory, since its proposal by Prevost, has been developed by Prevostaye and Desains, and more recently by the author of this work and by Kirchhoff. It will, perhaps, best conduce to clear conception if at first we assume the truth of this hypothesis, and then deduce its legitimate conclusions, shewing at the same time that these are all sup-

ported by experiment. Deferring until next chapter a proof in favour of the theory derived from the laws of cooling as ascertained by Dulong and Petit, let us for our present purpose imagine to ourselves a chamber of the following kind.

198. Let the walls which surround this chamber be kept at a constant temperature, say 100°C , and let them be covered with lamp-black—a substance which reflects no heat, or at least very little ;—also let there be a thermometer in the enclosure. It is well known that this thermometer will ultimately indicate the temperature of the surrounding walls, and that it will be a matter of indifference whether it be hung in the middle of the enclosure or at one of the sides ; in whatever part of the enclosure this instrument is placed its indication will be precisely the same, namely 100°C . (In what follows it ought to be *clearly borne in mind* that we are now supposing the theory of exchanges to be true, according to which bodies even of the same temperature are always giving and receiving radiant heat.)

EQUILIBRIUM OF HEAT RAYS.

199. **Heat equilibrium of surfaces.** Suppose that the outside of the bulb of the thermometer of the last article is covered with tinfoil, so that its reflecting power is considerable. Now according to the theory of exchanges this thermometer is constantly radiating heat towards the lamp-black, but it is receiving back just as much as it radiates. Let us call the radiation of lamp-black 100, and suppose that 80 of these 100 rays which strike the thermometer are reflected back from its tinfoil surface, while the remaining 20 are absorbed. Since therefore the thermometer is absorbing 20 rays, and since nevertheless its temperature is not rising, it is clear that it must also be radiating 20

rays, that is to say, *under such circumstances its absorption and radiation must be equal to one another.*

If we now suppose the outside of the bulb to be blackened instead of being covered with tinfoil, the thermometer will absorb nearly all the 100 rays that fall upon it, and just as in the previous case, since its temperature is not rising, it must be radiating 100 rays.

Thus we see that when covered with tinfoil it only radiated 20 rays, but when blackened it radiates 100. The radiation from a reflecting metallic surface ought therefore, if our theory be true, to be much less than from a blackened one. This has been proved experimentally by Leslie, who shewed that *good reflectors of heat are bad radiators.*

200. Again, we have seen that in the case of the bulb covered with tinfoil 80 of the 100 rays which fell upon it were reflected back, and we have also seen that 20 rays were radiated by the bulb. Hence the heat reflected *plus* the heat radiated by this thermometer in the imaginary enclosure will be equal to 100, that is to say, it will be equal to the lamp-black radiation from the walls of the enclosure. We may generalize this statement by saying that *in an enclosure of constant temperature the heat reflected plus the heat radiated by any substance will be equal to the total lamp-black radiation of that temperature*, and this will be the case whether the reflecting substance be placed inside the enclosure or whether it form a part of the walls of the enclosure. In fact, we may conceive the walls of such an enclosure to be formed of every variety of substances from polished metal to lamp-black, and yet the total flow of radiant heat coming from one portion will be the same as that coming from another portion, the only difference being that in the case of a reflector, such as the thermometer with tinfoil, this heat is partly radiated and partly reflected,

while in the case of lamp-black it is altogether radiated, the reflected heat being insensible.

The statement that the heat reflected *plus* the heat radiated by any substance in an enclosure of constant temperature will be equal to the total lamp-black radiation of that temperature has been experimentally verified by MM. Provostaye and Desains, who found—

Radiation from polished silver at a given temp.	= 2.2
Reflexion by silver of rays (represented by 100)	
from lamp-black at this temperature	= 97.0
Sum	= 99.2

Now 99.2 comes very near the lamp-black radiation, or 100.

They also found that the sum of the reflected and radiated heat from glass at different angles was equal to 93.9 (lamp-black radiation being equal to 100); and the difference between 93.9 and 100 they supposed to be due to diffuse reflexion.

201. Let us now once more return to our chamber of constant temperature, and imagine the thermometer carried from one part of the chamber to another where the surface is of a different shape.

We may, for instance, pass from Fig. 49, where the thermometer *T* is at the centre of a sphere, to Fig. 50, where it is within an acute angle. In the first case, the rays which reach the instrument will be those which have been emitted by the surrounding spherical envelope in a direction perpendicular to the surface; but in the latter case, most of the rays reaching the thermometer will have been emitted

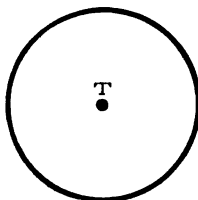


Fig. 49.

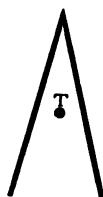


Fig. 50.

in an oblique direction. Yet the thermometer receives precisely the same amount of heat in both cases, and will always do so, whatever be the shape of the surrounding enclosure.

In fine, in such an enclosure streams of heat may be supposed to be passing and repassing in every possible direction, and to be equally intense in all directions, without the least regard to the shape or substance of that part of the enclosure from which they come.

Thus the stream of radiant heat impinging upon the surface AB (Fig. 51) in the direction CA perpendicular to AB will be the same whether it be supposed to proceed from a surface CD parallel to AB or from a surface CE inclined to AB . It thus appears that in our hypothetical enclosure of constant temperature the heating effect of a stream of heat is solely dependent upon its cross section,

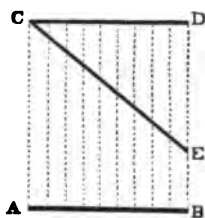


Fig. 51.

that is to say, upon the extent of surface AB perpendicular to its direction which it will exactly cover. This result has been verified experimentally by Provostaye and Desains; these observers having found, as we have already said, that the sum of the reflected and radiated heat from glass at different angles is a constant quantity.

When the source of the rays is a non-reflecting substance such as lamp-black, the statement of this law is very simple. We see from Fig. 51 that the heat which leaves the surface CD in the direction CA is precisely equal to that which leaves the surface CE in the same direction.

Hence the heat which radiates from a surface of lamp-black in any direction is proportional to and may be represented by the projection of this surface upon a plane perpendicular to the direction of the rays.

This result has been experimentally proved by Lambert of Berlin and also by Leslie, who made observations upon the heat from blackened surfaces at different angles.

The method of observation is very simple. Fig. 52 represents the arrangement, where *A* is an aperture behind which the heated body is placed. Now if this body be a blackened surface, it is quite immaterial whether it be

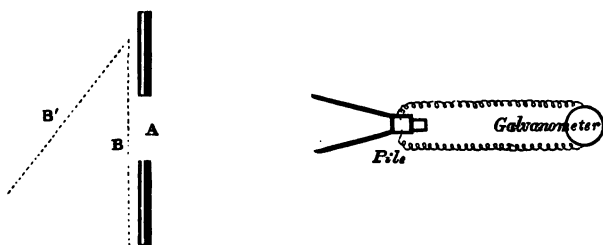


Fig. 52.

placed in the position *B* or *B'*, provided it be large enough to fill up, in the latter position, the field of view from the cone; in both cases the galvanometer attached to the pile will give the same indication. Undoubtedly, when the surface is in the position *B'*, a greater extent of this will be viewed by the cone; but as far as radiant heat is concerned, we may imagine the surface to be projected upon the aperture *A*, so that if the field behind this aperture be filled up by the blackened surface its inclination or curvature is of no consequence.

The same result would take place if for the sensitive pile we substitute the human eye, and for *B* a red-hot plate. For if such a plate always fills up the field of view behind this aperture *A* the result to the eye will be independent of its curvature and inclination, and in all cases the aperture will appear as a red-hot field, of the same intensity.

202. We have seen that the stream of radiant heat which strikes upon the thermometer in our enclosure of constant temperature is independent both of the materials and of the shape of the walls of the enclosure, so that if the instrument be carried from one part to another there will be no change in the amount of radiant heat falling upon it. Something more however is necessary, for we must not only have the *quantity* of heat which falls upon the thermometer the same throughout, but the *quality* of this heat must also remain the same. It will be necessary to give a short explanation of the word '*quality*.' It is well known that different kinds or qualities of light affect the same substance in different ways; thus red glass will absorb green light while it will allow red light to pass. In like manner there are a great many different kinds of dark heat, and the same substance will absorb some of these much more rapidly than others. So also heat as well as light may be polarized, and we have already seen (Art. 193) that a substance such as tourmaline absorbs heat polarized in one plane with greater intensity than heat polarized in a plane perpendicular to the former.

Now the word '*quality*' is here taken to denote *any specific peculiarity, whether of wave length or polarization*, which causes rays of heat to be differently absorbed by any substance.

When we say therefore that two pencils of heat are of the same quality, we mean that the mixture of wave lengths in the one is precisely the same as in the other, and also that the polarization of both is the same.

Suppose now that our thermometer is covered with some substance which displays this selective absorption for certain kinds of heat, and that we carry it about from one part of the enclosure to another. It will not only be necessary that the *quantity* of radiant heat which beats

upon our thermometer shall be the same throughout the enclosure, in order that the instrument may preserve its constancy of temperature, but the *quality* of this heat must also be the same; for if not, we might suppose that in one place the heat is of a kind that is greedily absorbed by the coating of the bulb, and that in another place it is of a kind that is reflected back from this coating; thus although the quantity of heat falling on the bulb might be the same in both places, yet the thermometer would absorb more in the first case than in the second, and its constancy of temperature would be destroyed. It is therefore clearly necessary that the stream of radiant heat which beats against the thermometer as it is carried about in the enclosure should be the same at all places, both as to *quantity and quality*.

Various experiments go to prove this uniformity both in the quantity and quality of the heat from different parts of an enclosure of constant temperature. Perhaps the most striking of these is that when an enclosure is heated to a red or white heat the luminous rays from the different parts of this enclosure will be the same both in quantity or luminosity, and in quality or colour, and will depend only on the temperature, and not on the nature of the materials composing the walls of the enclosure.

Again, as regards polarization, certain experiments by Provostaye and Desains appear to shew that the stream of heat in an enclosure of constant temperature is unpolarized, and that if there be a reflecting substance in the enclosure, so that the reflected portion of the heat from it is polarized, then the radiated heat from this substance will be polarized in the opposite way, so that the whole heat reflected and radiated together is unpolarized.

203. We are now in a position to extend the remark already made (Art. 199) with regard to the equality of the

absorption and radiation of a surface in our hypothetical enclosure. Such a surface must not only give back by radiation to the general stream of heat as much as it withdraws by absorption, but what it gives back must be of the same quality as that which it withdraws. The absorption of such a surface will therefore be equal to its radiation, and this equality will hold for every individual kind of heat of which the whole heterogeneous radiation is composed.

204. We deduce therefore, as the result of our inquiries, both theoretical and experimental, in this branch of our subject, that in an enclosure of constant temperature—

1. *The stream of radiant heat is the same throughout, both in quantity and quality; and while it depends on the temperature it is entirely independent of the materials or shape of the enclosure.*

2. *This stream is unpolarized.*

3. *The absorption of a surface in such an enclosure is equal to its radiation; and this holds for every kind of heat.*

205. **Heat equilibrium of plates.** Returning once more to our chamber of constant temperature, let us suspend in it a thin plate of rock salt. Now since the temperature of this plate remains constant, the plate must radiate just as much heat as it absorbs. But rock salt (Art. 191) absorbs very little heat hence also it will radiate very little. Moreover, a thick plate will absorb more than a thin one, and hence also it will radiate more. Both of these conclusions have been verified by the author of this work. By making use of the thermo-pile he has found that the radiation from a thin plate of rock salt is only 15 per cent. of the total lamp-black radiation for the same temperature, and that the radiation from a thick plate of rock salt is greater than from a thin one.

206. Suppose, however, that instead of rock salt we had

suspended two plates of glass of unequal thickness. Since this substance is extremely athermanous, that is to say opaque for heat, either of these plates would probably absorb nearly all the heat which fell upon it, and hence the radiation of both plates (radiation being equal to absorption) would be sensibly the same, and would be very great—in fact it would be much the same as if they stopped the whole heat, or were covered with lamp-black.

207. From this we see what it was that misled the early experimentalists on this subject, and induced them to think that radiation was confined, if not to the surface of a body, at least to a very small depth beneath it. They found that when a metallic surface was coated with varnish its radiative power was very much increased, but that very soon this increase attained its maximum, after which an additional coating produced no further effect. But the reason of this was, not that radiation is in all cases confined to a very small distance beneath the surface, but that these coatings were of a very athermanous substance, so that a very small thickness was practically equivalent to a surface of lamp-black. Could it have been possible to have applied a coating of transparent rock salt, the result would have been very different.

208. Let us now take our thermometer and cover its bulb once more with a substance having a selective absorption for heat, and, further, let us hang up before it in the enclosure a plate of rock salt. No change in the indication of the thermometer will take place; but in order that the temperature of this thermometer may remain without change it is obviously necessary that this plate of rock salt should change neither in quantity nor in quality the stream of heat which impinges against the bulb; that is to say, this stream after it has passed through the plate must be precisely the same both in quantity and in quality as

before it entered it. For if the stream of heat after having passed the rock salt were to be changed in quality though not in quantity, it would nevertheless affect differently the bulb of the thermometer which we have imagined to be coated with a substance having a selective absorption for heat. But in order that the rock salt may not change the quality of the stream of heat which passes through it, its absorption must be equal to its radiation for every kind of heat.

This result has likewise been verified experimentally by the author of this work. If the kind of heat which rock salt absorbs be the same as that which it radiates, it would follow that a cold plate of rock salt ought to be exceedingly opaque to the radiation from heated rock salt. That is to say, if in heated rock salt there be a plentiful radiation of a peculiar kind of heat, in cold rock salt there ought to be a plentiful absorption of this very heat. Now this was found to be the case. A moderately thick plate of this substance was found to stop at least three-fourths of the heat from a thin plate of heated rock salt, whereas it will only stop a small proportion of ordinary heat.

209. This affords an explanation of the fact that two plates of rock salt placed the one behind the other (equivalent to a single plate of double thickness) do not radiate twice as much as a single plate. For let EF be the front surface of such a double plate, of which CD represents a line midway between the two surfaces. Now, while as much heat will cross the line CD from the

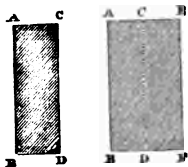


Fig. 53.

hinder half of the plate as would be radiated from the single plate $ABDC$, a great proportion of this heat (probably three-fourths) will be absorbed by the front half in its passage through it, since we have seen that rock salt absorbs

intensely the heat which it radiates. Hence, if the radiation of the single plate be 1, that of the double plate, instead of 2, will probably not be more than $1\frac{1}{2}$.

210. Our readers will thus be prepared to see that radiation is a thing which goes on in the interior of a plate just as much as near the surface; and they will also see that it does not necessarily follow from this that the radiation of a plate should be proportional to its thickness, but very much the reverse;—indeed, had the substance of the plate in Fig. 53 been glass instead of rock salt, the single plate would have given out sensibly the same amount of heat as the double plate, since in the latter the heat from *ABDC* would all have been stopped by *CDFE*. We are thus prepared to see that *in the interior of substances, as well as in air or in vacuo, a stream of radiant heat is constantly passing and repassing in all directions, and in the case of constant temperature, as this stream of heat passes any layer of particles it is just as much diminished by the absorbing action of these particles as it is recruited by their radiation, so that the stream flows on virtually unchanged both in quantity and quality until at last it reaches the surface.*

211. **Amount of internal radiation.** We have now to consider a more difficult question, which may be thus stated. Supposing we have several different substances all remaining at the same constant temperature, will the streams of radiant heat continually passing and repassing in the interior of these substances be equal to each other? In the first place, and before attempting to answer this question, we must shew how the intensity of a stream of radiant heat may best be measured. For this purpose let us suppose a small square surface representing unity of area to be placed in the interior of an enclosure, or of a substance surrounded by an enclosure kept at an uniform temperature. In accordance with the theory of exchanges,

streams of radiant heat will be continually passing through this surface in all directions; let us confine our attention to those rays, which are as nearly as possible perpendicular to the plane of our square unit. But it may be said, why not confine our attention to rays strictly perpendicular to this plane? In answer to this, we remark that in our present investigation (the reason will afterwards appear) we must regard a ray in the sense in which a straight line is regarded. And just as a line is in reality always part of the boundary of a solid, so a ray is always in reality part of the boundary of a beam or pencil of light. We may satisfy ourselves that this is the case in nature by considering the light which reaches the eye from a star or other object apparently very small; this would seem to be the nearest approach to a geometrical line of light; nevertheless, since a star has a certain real though very minute angular diameter, the light from it to a point of the eye is in reality a converging pencil, although no doubt the angle of convergence is very small.

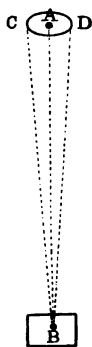


Fig. 54.

We will confine our attention therefore to rays as nearly as possible perpendicular to our unit area. Let B (Fig. 54) represent this area, and let CBD be a very small pencil or cone of rays nearly perpendicular to the plane of B , the central line AB being strictly perpendicular to this plane. Now if we suppose the angle CBD as well as our unit area to remain constant while we pass from one substance to another, then the quantity of heat radiated in an unit of time upon this unit area B through directions comprised within the small cone CBD may be taken to denote the intensity of internal radiation of the substance in question.

212. The circle CAD may in fact be compared to the

disk of a small star whose diameter CD subtends with the eye the angle CBD (greatly exaggerated in the diagram for the purpose of demonstration), and from which a beam or pencil of light represented by the cone CBD reaches the eye of the terrestrial observer at B . Now imagine, for the sake of demonstration, that it is possible to place the eye in the interior of a substance of constant temperature, and also that the eye is sensible to all the rays which compose, according to our hypothesis, the entire radiation of the substance, then it is evident that if the eye look in the direction of CAD , the *brightness* of the field of view in front of the eye or of any given detached portion of this field, such as the area CAD , will indicate the internal radiation ; so that, if the eye be now removed to the interior of another substance of greater internal radiation, more rays will strike it in front from CAD in one second of time, and the field of view will therefore appear brighter in the very same proportion in which the internal radiation is increased.

213. Let us now direct our attention to an enclosure, such as a sphere (Fig. 55), kept at a uniform temperature, and suppose the lower half of this enclosure to be filled with an uncrystallized solid, or liquid (index of refraction = μ) while the upper half is a vacuum. Let us also suppose that

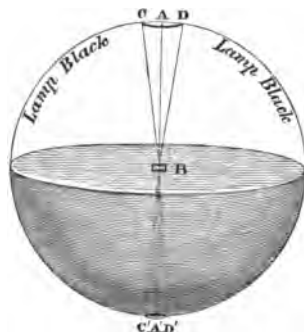


Fig. 55.

the external boundary of this upper half of the sphere is covered with lamp-black, and let the area B be now placed on the surface of the solid or liquid, while the area CAD is a very small circle approximately coinciding

with the lamp-black boundary of the sphere. Let us denote by R the radiation of lamp-black, that is to say, let R represent the number of heat rays which *reach* the unit area B through the directions of the cone CBD in one second of time.

214. Part of these rays *reaching* B will be reflected back ; let us call this reflected portion aR ; then $R - aR$, or $(1 - a)R$, will denote the amount of these rays which *really penetrate* the medium in one second of time. But these rays will be bent by refraction towards the perpendicular, after entering the medium, and will therefore be comprised in a cone $C'BD'$ with a smaller angle than CBD .

The angle $C'BD'$ may very easily be found ;—for

$$\frac{\sin CBA}{\sin C'BA'} = \mu ;$$

or, since these angles are very small,

$$\frac{CBA}{C'BA'} = \mu, \text{ or } \frac{CBD}{C'BD'} = \mu.$$

We thus see that of the rays under consideration a portion equal to $(1 - a)R$ *enters* the substance, and is after its entrance embraced in a cone of which the angle

$$C'BD' = \frac{CBD}{\mu}.$$

215. But since the substance we are considering, being of constant temperature, gains as much heat as it loses in all of its parts, it follows that as much heat must *pass out* by B along lines embraced within the cone $C'BD'$ as *passes into* the substance through these same directions. Hence the quantity of heat which will *pass out* of the substance by B along lines embraced within a cone having the angle $C'BD'$ will (for one second of time) be $(1 - a)R$.

216. Now let R' be the unknown internal radiation for

the medium ; that is to say, let R' denote the quantity of heat rays which will in one second reach B from the interior in directions comprised within a cone which has a constant standard angle equal to CBD (Art. 211). We must find what fraction of this radiation will reach B if the angle be CBD' instead of CBD . It is evident that the amount of heat reaching B through the directions of the cone CBD will be proportional to the area CAD , and this area will be proportional to the square of CD , and very nearly to the square of the angle CBD . Hence—

$$\text{Heat through } CBD' : \text{heat through } CBD (=R') :: (CBD')^2 : (CBD)^2.$$

Therefore

$$\text{Heat from interior through } CBD' = R' \times \left(\frac{CBD'}{CBD} \right)^2 = \frac{R'}{\mu^2} \text{ by Art. 214.}$$

We thus see that a quantity of heat $= \frac{R'}{\mu^2}$ will in one second of time reach B from the interior through the cone CBD' . But of this heat we know from the laws of optics that the amount $\alpha \left(\frac{R'}{\mu^2} \right)$ will be reflected back into the interior, and hence $(1-\alpha) \frac{R'}{\mu^2}$ will be the heat which *passes out* through B through the cone CBD' .

217. We have thus obtained two expressions, one for the heat which enters the substance through B and diverges through the directions of the cone CBD' , namely $(1-\alpha)R$ (Art. 214), and the other for the heat which passes out through B through the same cone, namely $(1-\alpha) \frac{R'}{\mu^2}$; and we have seen (Art. 215) that these two expressions must be equal to one another.

$$\begin{aligned} \text{Hence } (1-\alpha) R &= (1-\alpha) \frac{R'}{\mu^2}; \\ \therefore R' &= \mu^2 R. \end{aligned}$$

That is to say, the internal radiation in a substance of which the index of refraction is μ will be $\mu^2 R$, R denoting the radiation of lamp-black corresponding to the temperature of the experiment.

It is also clear from what we have said that this relation will hold for every individual description of heat of which the whole radiation is composed.

EQUILIBRIUM OF LIGHT RAYS.

218. It is of importance to extend these observations to radiant light, or, in other words, to those rays which affect the eye, and this extension has been made both by Professor Kirchhoff of Heidelberg and by the author of this work.

We have already endeavoured to accumulate evidence in favour of the opinion that radiant light and heat are only varieties of the same physical agent, differing from one another simply in wave length; but during the progress of this branch of science many inquirers have been inclined to think that light and heat are physically distinct, although possessing many properties in common, and it has even been imagined that some kinds of light are entirely destitute of any heating effect.

But if it can be shewn that the consequences of Prevost's theory extend to radiant light, we are furnished with very strong evidence in favour of that hypothesis which regards heat and light as varieties of the same agent.

219. Prevost's theory consists of the three following statements.

1. If an enclosure be kept at a uniform temperature, any substance surrounded by it on all sides will ultimately attain that temperature.
2. All bodies are constantly giving out radiant heat, at

a rate depending upon their substance and temperature, but independent of the substance or temperature of the bodies that surround them.

3. Consequently when a body is kept at uniform temperature it receives back just as much heat as it gives out.

From these statements follow all the laws that have been deduced for radiant heat. But in the process of argument it is essential to regard the rays under consideration as being capable of heating the bodies on which they fall and by which they are absorbed.

Hence, if this theory extend to light, it is highly probable that luminiferous rays are capable also of heating more or less the bodies by which they are absorbed.

The following experiments exhibit the extension of the theory of exchanges to rays of light.

220. Light equilibrium of surfaces. It has been shewn with respect to Heat (Art. 199) that good reflectors are bad radiators, and a similar experiment may be made for light. Thus if a pot of red-hot lead or tin be carried into a dark place and the dross skimmed aside by a red-hot iron ladle, the liquid metal will appear less luminous than the surrounding dross. Also if a piece of platinum partly polished and partly tarnished be held above the flame of a Bunsen's burner in a dark room, the tarnished portion will shine much more brilliantly than the polished. A very good arrangement, suggested by Professor Tait, is to heat thus a piece of platinum foil with an ink-mark on it.

Another variety of the same experiment is to mark a black poker with chalk, and, if the poker at a good red heat be then viewed in a dark room, the marked parts will appear comparatively non-luminous.

Finally, if we take a piece of stoneware of a black and white pattern, heat it to redness and then view it in the dark, the black will shine much more brightly than the

white, presenting a very curious reversal of the pattern, which we have endeavoured to delineate in Figures 56 and 57.



Fig. 56.

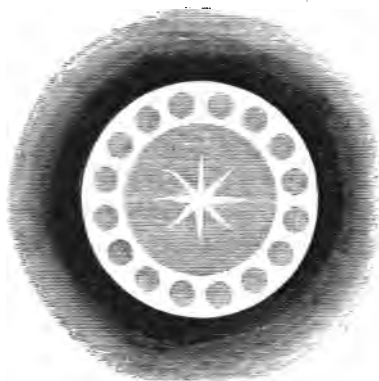


Fig. 57.

221. Light equilibrium of thin plates. *Experiment I.*

—If a piece of colourless transparent glass be heated to redness in the fire, removed to the dark, and then viewed, it will be found to give out very little light; but if the glass be coloured, its light radiation will be more copious, the amount of light given out depending upon the depth of colour. This is an experiment analogous to that with rock salt, and it is evident that the colourless glass gives out but little light because it absorbs but little. A stratum of heated air may likewise be instanced as a substance which neither absorbs nor emits light or heat to a sensible degree.

222. *Experiment II.*—It has been shewn that the heat radiated by a thin plate of any substance at a given temperature is precisely that kind of heat which the plate absorbs when heat of that temperature is allowed to fall upon it. Now the same thing holds with regard to light.

With respect to the rays proceeding from an ordinary fire, all coloured glasses may be divided into two groups, those which redden and those which whiten the fire as we look through them. The first group comprises red and orange glasses, and these absorb the whiter descriptions of light; the second group comprises green and blue glasses, and these absorb the redder kinds of light. We should therefore expect red and orange glasses to give out, when heated, a peculiarly white light, and green and blue glasses a peculiarly red light. Now this is found to be the case. A red glass coloured by gold, when heated to redness, removed, and viewed in the dark, gives out a milky-white or even greenish light, and the orange glasses used by photographers do the same. On the other hand, green and blue glasses give out, when thus heated, a reddish kind of light. This experiment is analogous to that wherein it is shewn that a cold plate of rock salt stops a large proportion of the heat from a hot plate of the same substance.

223. *Experiment III.*—Again, we know (Art. 193) that when a ray of ordinary light falls upon a plate of tourmaline cut parallel to the axis, it absorbs nearly all that resolved portion of the rays which is polarized in a plane parallel to the axis of the crystal, while it allows to pass a considerable portion of those rays which are polarized in a plane perpendicular to the axis. Now it can be shewn that if such a plate be heated red hot, the rays of light which it gives out are partially polarized in the same direction as those which it absorbs, viz. in a plane parallel to the axis. This experiment may best be tried by a method devised by Professor Sir George Stokes, in which a hollow cast-iron bomb is heated to redness. This bomb is represented in Figures 58 and 59. In Figure 58 we see it as it appears from the outside, with small holes by which we can see into

it. Fig. 59 represents a section through the centre of the bomb, shewing the tourmaline *T* attached to a stand, *C* denoting the moveable lid. This tourmaline passes through the very centre of the bomb, and hence in looking through the bomb, by means of the small holes, the eye encounters the plate of tourmaline. Now let this bomb be heated to redness, having the tourmaline inside of it, and be then taken out of the fire and placed in the dark. The tourmaline will cool very slowly in this position, since



Fig. 58.

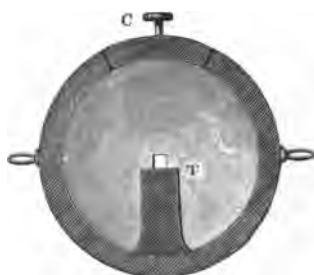


Fig. 59.

it is (with the exception of the small hole) entirely surrounded by a red-hot enclosure, viz. the interior of the bomb, which, if the iron be sufficiently thick, will remain hot for some time. Now the eye in looking through the bomb by means of the small hole will encounter the radiated light from the heated tourmaline, and by means of a polariscope it is easy to ascertain in what plane this light is polarized. It will be found to be polarized in a plane at right angles to that in which light is polarized as it passes through the same tourmaline when cold and similarly placed.

224. Experiment IV.—We have seen that in an enclosure of uniform temperature the flow of radiant heat is the

same in all directions, both as regards quantity and quality, whatever be the substances with which the enclosure is filled. Now with regard to light a good coal fire may be viewed as an enclosure of approximately uniform temperature, and accordingly we ought to find that, whatever substances be put into this fire, when these ultimately become of the same temperature as the fire, they will not alter the nature of the light which is given out. We may prove this by throwing coloured glasses into the fire, and when these become sufficiently heated they will be found to have lost all their colour. The red glass, for instance, which we have thrown in will, as we have already seen, give out a greenish light on its own account; but it will pass red light from the coals behind it in such a manner that the light which it radiates precisely makes up for that which it absorbs; so that we have *virtually a coal radiation* coming partly from and partly through the glass.

225. We cannot conclude this subject without alluding to a very interesting experiment first made by Foucault, but afterwards revived and extended by Kirchhoff, in which the equality between radiation and absorption is extended to individual rays of the spectrum.

Foucault found that the voltaic arc formed between charcoal points often emits the ray *D* of the solar spectrum on its own account, and at the same time absorbs it when it comes from another quarter. Kirchhoff, again, found that coloured flames, in the spectra of which bright sharp lines present themselves, weaken rays of the colour of these lines when such rays pass through the flames. We thus see that the same media which in a heated state emit rays of a certain refrangibility in great abundance have also the power of stopping these rays when they fall upon them from another source.

CONCLUDING REMARKS.

226. We have thus arrived both theoretically and experimentally at a law which may be enunciated as follows :—

Bodies when cold absorb the same rays which they give out when hot. The reader will at once be struck with an analogy between sound and light in this respect. A musical string when at rest takes to itself and therefore absorbs the very note (given out by another instrument) which it will itself give out when in a state of vibration.

Reasoning from this analogy Sir George Stokes had suggested beforehand the probability of a connexion between the absorption and radiation of bodies for particular rays of the spectrum, and he also imagined that this suggestion would account for the dark lines in the solar spectrum.

The prediction of this philosopher has been abundantly confirmed by the labours of Kirchhoff; but the striking conclusions with regard to the constitution of the sun and stars which Kirchhoff has experimentally arrived at must be deferred till another chapter.

We cannot, however, refrain from remarking that the law developed in this chapter affords a valuable confirmation by analogy of the truth of the undulatory theory of light. The likeness between a vibrating string and a heated particle has been remarked above, and we have seen that a particle (just as a string with regard to sound) absorbs the same kind of ray which it gives out. It is, perhaps, allowable to infer that light, like sound, consists of undulations which are propagated in a medium surrounding bodies, and that when heat or light is absorbed by a particle, the motion is conveyed from the medium to the particle, just as, when a string takes up a note passing through the air, the motion is conveyed from the air to the string ;

and that, again, when heat or light is radiated by a particle it is similar to the giving out by a string of its note to the air.

CHAPTER IV.

Radiation at Different Temperatures.

227. It has already been stated (Art. 204) that the stream of radiant heat continually proceeding through an enclosure of which the walls are kept at a constant temperature depends only on the temperature of the walls, and not on the nature of the various substances of which they are composed; the only difference being that for metals this stream is composed partly of radiated and partly also of reflected heat, while for lamp-black it is composed wholly of radiated heat. This may be expressed by saying that this stream depends upon or is a function of the temperature, and of it alone; but there is the following very important difference between a reflecting and a lamp-black surface, as representing this stream of radiant heat.

It is only when a reflecting surface forms part of a *complete enclosure* of the same temperature as itself, that the radiated and reflected heat from this surface together represent the whole stream of heat; for if we bring it for a moment into another enclosure of lower temperature, the reflected heat is altered, and although the radiation will for a short time continue nearly constant, yet this radiation will not represent the whole stream of heat due to the temperature of the surface.

On the other hand, if a lamp-black surface be placed in the above position, since the stream of heat which flows from it is entirely independent of the reflexion due to neighbouring bodies, the heat which it radiates when brought

for a moment into an enclosure of lower temperature than itself will truly represent the stream of radiant heat due to the temperature of the lamp-black.

228. Suppose now that we have a thermometer with a blackened bulb, and that this is placed in a blackened vacuous enclosure of a lower temperature than itself; the heat which it radiates will represent the total radiation due to the temperature of the bulb, while that which it receives will represent the total radiation due to the temperature of the enclosure, and the difference between these two will denote the loss of heat experienced by the thermometer.

Thus, if θ be the temperature of the enclosure, and $t + \theta$ that of the bulb, then, since the stream of radiant heat (Art. 204) is a function of the temperature only, we shall have this stream represented by $F(t + \theta)$ and $F(\theta)$ for these two temperatures, and the rate at which the thermometer loses heat will be denoted by $F(t + \theta) - F(\theta)$.

This is the rate at which the instrument loses radiant heat, and it will also represent the rate at which it loses temperature, or the velocity of cooling, as this is termed, if we suppose that the specific heat (or heat required to produce a change of 1°) of the mercury of the thermometer remains the same for all the temperatures of the experiment. This, though not precisely, is very nearly the case, and hence the velocity of cooling of a thermometer placed in these circumstances may be regarded as representing with great accuracy the intensity of radiation.

VELOCITY OF COOLING; VARIATION WITH TEMPERATURE OF 'QUANTITY' OF RADIATION.

229. Newton was the first to enunciate his views on the cooling of bodies. He supposed that a heated body exposed to a certain cooling cause would lose at each instant a quantity of heat proportional to the excess of its tempera-

ture above that of the surrounding air. It was, however, soon found that this law was not exactly followed, and several philosophers made experiments on the subject, with more or less success, until the time of MM. Dulong and Petit, who made a very complete and successful investigation of the velocity of cooling of a thermometer both in vacuo and in air. Let us now describe their experiments in vacuo.

230. The apparatus used by these experimenters consisted of a hollow globe of thin copper, with the interior blackened, which could be immersed in a vessel of water or other liquid of known temperature. Through an orifice in this globe a thermometer could be inserted, so as to have its bulb in the centre of the globe. The temperature of this thermometer was always higher than that of the globe, and the number of degrees through which the mercury was observed to sink in a minute, supposing its rate of cooling to be uniform during that time, was taken to denote the velocity of cooling of the thermometer.

A preliminary set of experiments was first made, from which it appeared that the *law of cooling* of a liquid mass is independent of the nature of the liquid and of the form and size of the vessel which contains it. Having determined this, MM. Dulong and Petit proceeded to make their final experiments with a large thermometer containing about 3 lbs. of mercury inserted in the centre of their globe. The temperature of the globe was kept as nearly as possible uniform during the course of an experiment. In the first instance this thermometer preserved its natural vitreous surface, and the number of degrees through which its mercurial column fell in one minute was considered to denote the velocity of cooling of the thermometer corresponding to its average temperature during that minute.

The following were the results obtained where the temperature of the enclosure was that of melting ice.

Excess of temperature of the thermometer. °C.	Velocity of cooling. °C per min.
240	10.69
220	8.81
200	7.40
180	6.10
160	4.89
140	3.88
120	3.02
100	2.30
80	1.74

We see at once from this table that the law of Newton does not hold, for according to it the velocity of cooling for an excess of 200° should be precisely double of that for an excess of 100°: now we find that it is more than three times as much.

231. In Dulong and Petit's experiments the excess of temperature of the thermometer and also the actual temperature of the enclosure were made to vary, that is to say, both t and θ varied; and they obtained the following results

Excess of temperature of thermometer.	Velocity of cooling, for various temperatures of enclosure.				
	$\theta = 0^{\circ}\text{C.}$	$\theta = 20^{\circ}\text{C.}$	$\theta = 40^{\circ}\text{C.}$	$\theta = 60^{\circ}\text{C.}$	$\theta = 80^{\circ}\text{C.}$
(t)					
240	10.69	12.40	14.35	...	...
220	8.81	10.41	11.98	...	...
200	7.40	8.58	10.01	11.64	13.45
180	6.10	7.04	8.20	9.55	11.05
160	4.89	5.67	6.61	7.68	8.95
140	3.88	4.57	5.32	6.14	7.19
120	3.02	3.56	4.15	4.84	5.64
100	2.30	2.74	3.16	3.68	4.29
80	1.74	1.99	2.30	2.73	3.18
60	...	1.40	1.62	1.88	2.17

Now if we divide the numbers of the third column by the corresponding numbers of the second—for instance, 12.40 by 10.69—we find the quotient to be 1.16; and continuing the process for the other numbers in these columns, we find:—

$\frac{\text{3rd column}}{\text{2nd column}}$ gives as quotients, 1.16, 1.18, 1.16, 1.15,
1.16, 1.17, 1.17, 1.18, 1.15.

In like manner

$\frac{\text{4th column}}{\text{3rd column}}$ gives as quotients, 1.16, 1.15, 1.16, 1.16,
1.17, 1.16, 1.17, 1.15, 1.16, 1.16.

$\frac{\text{5th column}}{\text{4th column}}$ gives as quotients, 1.15, 1.16, 1.16, 1.15,
1.17, 1.16, 1.18, 1.16.

$\frac{\text{6th column}}{\text{5th column}}$ gives as quotients, 1.15, 1.15, 1.16, 1.17,
1.16, 1.17, 1.17, 1.15.

These numbers are all nearly the same, and their mean is 1.165. Hence we see that corresponding numbers in the various columns form a geometrical progression; so that if we denote a number in the second column by unity, we shall have 1, 1.165, $(1.165)^2$, $(1.165)^3$, $(1.165)^4$, as representing the velocities of cooling for the same excess of temperature for the cases where the temperature of the enclosure is denoted by 0° , 20° , 40° , 60° , 80° .

We are thus entitled to say that *the velocity of cooling of a thermometer in vacuo for a constant excess of temperature increases in a geometrical progression when the temperature of the surrounding medium increases in an arithmetical progression, and the ratio of this progression is the same whatever be the excess of temperature.*

232. MM. Dulong and Petit soon saw that this remark would enable them to find the law of cooling.

In the first place, it ought to be observed that the results already given are in accordance with the theory of exchanges, and that they form an additional proof of the truth of that theory. The theory of exchanges asserts that the loss of heat experienced by a thermometer cooling in vacuo is represented by the difference between the radiation due to the temperature of the thermometer and that due to the temperature of the enclosure. Hence, according to this theory, if A, B, C , denote the absolute radiation at the temperatures a, b, c , of which a is the highest and c the lowest, then

$A - B$ will represent the rate of cooling of a thermometer of temperature a in an enclosure of temperature b :

$B - C$ will represent the rate of cooling of a thermometer of temperature b in an enclosure of temperature c :

$A - C$, or $(A - B) + (B - C)$, that is to say, the *sum of the two preceding rates*, will represent the rate of cooling of a thermometer of temperature (a) in an enclosure of temperature (c) if Prevost's theory is true. Testing this by the table of Art. 231, we find that if $a = 140^\circ$ and $b = 80^\circ$ ($t = 60^\circ$, $\theta = 80^\circ$), then the velocity of cooling, $A - B$, is 2.17. Again, if

$$b = 80^\circ \text{ and } c = 20^\circ \text{ (} t = 60^\circ, \theta = 20^\circ \text{),}$$

the velocity of cooling, or $B - C$, is found to be 1.40. Hence the sum of these two rates will be

$$2.17 + 1.40 = 3.57.$$

Once more: if $a = 140^\circ$ and $c = 20^\circ$ ($t = 120^\circ$, $\theta = 20^\circ$), we find from the same table that the velocity of cooling, or

$A - C$, is 3.56. Now this is as nearly as possible equal to the sum of the two preceding rates, which was 3.57; so that the evidence derived from these experiments is decidedly in favour of the theory of exchanges.

Assuming therefore the truth of this theory, MM. Dulong and Petit supposed that the velocity of cooling of a thermometer in vacuo may be represented by the function $F(t + \theta) - F(\theta)$, where the first term represents the absolute radiation of the thermometer whose temperature is $t + \theta$, and the second term the counter-radiation of the enclosure whose temperature is θ .

233. Now we have seen (Art 231) that for an excess of temperature of 200° of the thermometer above that of the enclosure the velocity of cooling may be denoted thus—

Temperature of enclosure	= 0°C.	20°	40°	θ°
Velocity of cooling ($t = 200^\circ$)	= 7.40	$7.40(1.165)^{20}$	$7.40(1.165)^{40}$	$7.40(1.165)^\theta$
—	= 7.40	$7.40(1.0077)^{20}$	$7.40(1.0077)^{40}$	$7.40(1.0077)^\theta$

In like manner if t , or excess of temperature, = 180° we shall have—

Temperature of enclosure	= 0°C.	20°	40°	θ°
Velocity of cooling ($t = 180^\circ$)	= 6.10	$6.10(1.0077)^{20}$	$6.10(1.0077)^{40}$	$6.10(1.0077)^\theta$

It thus appears that for an excess = 200° we have 7.40 as a constant multiplier of the various terms, while for an excess = 180° this multiplier becomes 6.10. This multiplier varies therefore with the excess of temperature or t , but not with the temperature of the enclosure, or θ , if only the excess remains constant; it is therefore a function of t , and we may represent it by $\phi(t)$, according to the usual notation. Hence, writing a for 1.0077, we see that the velocity of cooling for any values of t and θ may be represented by

$$a^\theta \phi(t).$$

But the velocity of cooling (Art. 232) is also represented by

$$F(t + \theta) - F(\theta).$$

Hence these two expressions must be equal to each other, or

$$F(t+\theta) - F(\theta) = a^\theta \phi(t).$$

Putting $\theta = 0$ in this equation we obtain

$$F(t) - F(0) = \phi(t),$$

subtraction of which from the general equation gives

$$F(t+\theta) - F(\theta) - F(t) + F(0) = (a^\theta - 1)\phi(t).$$

Now in the left-hand expression t and θ may be interchanged without alteration of its value; consequently the right-hand side must contain the same function of t as of θ , and thus

$$\phi(t) = m(a^t - 1),$$

where m is a constant quantity.

The velocity of cooling of the thermometer in vacuo will therefore be represented by

$$F(t+\theta) - F(\theta) = ma^\theta(a^t - 1) = ma^{t+\theta} - ma^\theta$$

where $t+\theta$ is the temperature of the thermometer, and θ that of the enclosure in Centigrade degrees; and this further gives

$$F(\theta) = ma^\theta + k,$$

where k is a constant quantity at present undetermined.

The value of m in the present case is 2.037, as may be easily found from the table of results.

When the bulb of the thermometer was covered with silver it was found that the velocity of cooling might be expressed by the same formula, only with a change in the value of m . Here it was necessary to suppose $m = 0.357$.

234. We are thus led to suppose that the expression $m(1.0077)^\theta + k$, in which m varies from one substance to another, will represent the absolute radiation corresponding to the temperature θ ; this expression must nevertheless be considered as a mere empirical formula satisfying observation, which we are unable to deduce as a consequence from any

known properties of matter. In truth our knowledge of the forces concerned in radiation is very small.

But on closely examining Dulong and Petit's results M. Stefan was led in 1879 to conclude that the radiation emitted by a body is proportional to the fourth power of its absolute temperature (as defined later in Art. 343), or

$$F(\theta) = n(273 + \theta)^4,$$

the velocity of cooling in vacuo being therefore equal to

$$n\{(273 + t + \theta)^4 - (273 + \theta)^4\},$$

where n is a constant quantity; and this law has not only been theoretically deduced by M. Boltzmann, but is also in better agreement than that of Dulong and Petit with the results of more recent experiments by MM. Provostaye and Desains on the cooling of bodies.

235. Absolute measure of radiation. While the experiments of Dulong and Petit are admirably adapted to give the law of cooling, they are not so well fitted to determine in absolute measure the radiation from a heated body. A determination of this kind was made by Mr. Wm. Hopkins, who represented by unity the quantity of heat required to raise 1000 grains of water one degree Centigrade, and in terms of this unit measured the amount of radiant heat R which would be lost in *one minute* by a *square foot* of a given surface in vacuo. Putting

$$R = \mu a^\theta (a^t - 1),$$

where a , θ , t are as before, he obtained for μ the values given in the second column of the subjoined table; the numbers in the third column are the corresponding values of μ when R represents the heat lost in a *second* by a *square centimetre*, the unit of heat being that required to raise one gramme of water through one degree C.

Name of substance.	Values of μ .	
Glass.	9.566	.01112
Chalk (dry)	8.613	.01001
New red sandstone (dry)	8.377	.00974
Sandstone (building stone)	8.882	.01033
Limestone (polished)	9.106	.01059
Limestone (unpolished: same block)	12.808	.01489

VARIATION WITH TEMPERATURE OF QUALITY OF HEAT.

236. Having now considered the law of cooling as representing with much accuracy the *quantity* of heat given out by a black substance at different temperatures, we come next to the relation between the temperature and the *quality* or nature of the heat given out. And here we may remark that the laws which connect the radiation of a black body with its temperature, both as regards the quantity and the quality of the heat given out, hold approximately for bodies of indefinite thickness which are not black,—thus, for instance, they would hold for a metallic surface, which would represent very nearly a lamp-black surface with the radiation diminished a certain number of times.

These laws would not, however, hold exactly for a white surface, such as chalk; for this substance behaves like lamp-black with respect to rays of low temperature, while it is white for rays of high temperature, and the consequence of this will be that its radiation will increase less rapidly than that of a lamp-black surface. In like manner, these laws will not hold exactly for coloured surfaces.

Now with regard to a lamp-black surface, which, as we have seen, is the proper representative of heated surfaces, we have reason to believe that the following laws hold.

1. *The spectrum of the radiant heat and light given out by*

a lamp-black surface is continuous, embracing rays of all refrangibilities between certain limits on either side. Thus the spectrum of an ordinary fire is continuous; and in like manner that of the electric light, or of carbon at a very high temperature, is also continuous.

2. We have reason to think that as the temperature rises, the spectrum of a black substance is extended in the direction of greatest refrangibility, so as to embrace more and more of the violet and photographic rays.

This extension of the spectrum is also very perceptible to the eye, for a body at first emits only dark rays or rays of low refrangibility, then as its temperature increases it becomes red, and afterwards becomes yellow, and finally it becomes white.

There is thus a very apparent change with increasing temperature in the refrangibility of the radiation; and this is produced in the first place, as we have seen, by the addition of rays of high refrangibility, which are, at least as far as we can judge, absent from the radiation of lower temperature. But besides this, we are induced to believe that each individual ray of the low temperature is increased for the high temperature, only a ray of high refrangibility is increased in a greater proportion than one of low refrangibility, so that probably the average refrangibility is augmented at the same time that the total amount of radiation of any given refrangibility is also increased. Thus, the radiation from a piece of coal just below redness consists entirely of dark rays, while that from the sun embraces a large proportion of luminous and chemical rays, and is probably of a much higher average refrangibility than the radiation from the coal; but the dark rays common to both bodies likewise occur in greater amount in the solar radiation, where they form, in fact, a spectrum of great heating power towards the left of the red.

237. It thus appears that the rays proceeding from a heated body do not sensibly affect the human eye until the body has attained the temperature of redness, after which the body rapidly increases in luminosity. Thus, for a range of at least 500° Fahr. above the temperature of the eye the rays of heat emitted by a body are invisible. The cause of this invisibility is rather a physiological than a physical question; nevertheless, the suitability of this arrangement is at once apparent, for if any other law were to hold—if, for instance, the eye were affected by each substance in proportion to the difference between its radiation and that due to the temperature of the human body—it is difficult to conceive how we could either enjoy the advantages of darkness, or experience that variety of shade and colour which is one of the chief pleasures of vision. It is also worthy of remark that by the present arrangement our safety is secured, for the eye is generally able to detect the presence of combustion when it occurs.

RADIATION OF A PARTICLE; RADIATION OF GASES.

238. Having discussed the radiation from heated surfaces, we proceed to consider that from thin plates and particles. Take, for instance, a glass plate at a low temperature: this will stop nearly all the rays corresponding to this temperature, and therefore it will behave very much like a lamp-black surface. But at a high temperature (above redness, for instance) it will pass a great many of the rays of this temperature; and hence, its proportional absorption being less, its proportional radiation compared to lamp-black will also be less. The radiation of such a plate will not therefore increase with the temperature as fast as that from a lamp-black surface. Many other bodies besides glass possess the property of being more

opaque to heat of low than to that of high temperature, and for all these the radiation will not increase with the temperature so fast as that from a black surface.

The thinnest plates of solid or liquid substances which we can obtain will not, however, afford us the means of studying the radiation from a particle; in order to do this recourse must probably be had to a gas, each of whose particles we may perhaps suppose to act for itself, and not to be fettered by the neighbouring particles in the way in which it would be in the solid or liquid state.

239. In studying the radiation of gases we are led to some very peculiar laws.

1. In the first place, we may say that *the general absorption and radiation of gases are often small, while on the other hand the selective absorption and radiation of many of them are very strong.* The feeble radiation from heated air was observed by Melloni, and the feeble absorptive power of it, as of many other gases, for light is familiar to every one. Nevertheless, by aid of electricity we are enabled to heat a portion of any gas or vapour to a very high temperature, so as to obtain a visible spectrum from it, which we may then analyse by means of the spectroscope. Such spectra when obtained are generally discontinuous; that is to say, they consist of a very intense radiation of certain disconnected spectral rays, while the intervening spaces are totally, or nearly totally, dark.

2. In the next place, *the bright lines given out by any one gas do not as a rule coincide in spectral position with those given out by any other gas.* Certain coincidences of this kind are however supposed to exist, and of these we shall speak presently. Elaborate researches on the spectra of gases have been made by various experimenters.

3. In the third place, *the spectra of gases probably remain of the same character, with certain limitations to be afterwards*

mentioned, throughout a very wide range of temperature. We must make the following exception. If, for instance, one of the bright lines given out by a heated vapour be in the blue of the spectrum, and if this vapour be capable of existing at a red heat, we must not expect that it will give out the blue line at this heat, nor until the temperature rises to such a degree that blue becomes one of the constituent rays of that temperature. When this is reached the blue line will be given out, and when once given out it will probably continue throughout a great temperature range.

4. Fourthly. *An exception to this last law takes place when the incandescent vapour, from nearness of its particles, is in a state of complex molecular aggregation.*

Dr. Frankland has shewn that under sufficient pressure the gas hydrogen may be made to give out a spectrum approximately continuous.

Mr. Lockyer again has been led by his solar researches to the conclusion that gases or vapours which give out channelled spectra are in a state of comparative molecular complexity, while those that give out line spectra are in a state of molecular simplicity.

The more recent researches of Sir H. Roscoe, Dr. Schuster, Mr. Lockyer, and others lead us to believe that in the case of many gases there are several successive stages of spectral simplification as the temperature is increased. It follows from this that the absorption spectrum of a gas at a low temperature may be very different from its radiation spectrum at a high one.

5. Fifthly. *When a radiating particle is approaching the observer at a rapid rate, the wave lengths of the lines that it gives out are diminished, and when it is rapidly receding from the observer, the wave lengths of these lines are increased.*

This principle was first enunciated by Doppler. It was applied by Dr. Huggins as a method of ascertaining the

proper motions of the fixed stars in a direction to or from the earth, and by Mr. Lockyer and others in ascertaining the velocity of the meteorological motions in the atmosphere of the sun.

It is susceptible of easy illustration if we refer to sound. Let us, for instance, suppose that we have a locomotive at rest and whistling with a note which corresponds to 1100 blows given to the air each second of time. Now since sound travels, let us say, at the rate of 1100 feet per second, these various blows will follow each other one foot apart, the previous one having advanced through one foot at that moment when the next is given out, in other words, the wave length of the note is one foot. If however the locomotive is not at rest but moving in the direction of the sound at the rate, let us say, of 100 feet per second, it is evident that during the interval between two blows the locomotive itself, which is the source of the blows, will have advanced one-eleventh of a foot. Hence the blows will now be only ten elevenths of a foot apart, or the wave-length will have been diminished. In like manner had the engine been moving in an opposite direction, it might be shewn that the wave length would have been increased.

Inasmuch, however, as the velocity of light is very great compared to that of moving bodies, the amount of change produced by proper motion in the wave length of the rays emitted is in all cases comparatively small.

240. These laws of gaseous radiation have lately become of great practical importance. Let us recapitulate the most important of them.

In the first place, the spectrum of an ignited gas consists of a few bright lines of definite refrangibility.

Secondly, these lines are as a rule not the same for any two substances.

Thirdly, the lines peculiar to any substance remain the same throughout a great range of temperature.

If to these three laws we add the following chemical one, namely, that at a very high temperature most substances are decomposed, we shall soon readily perceive the great practical importance of this combination of facts.

For if we already know the spectra of the various chemical elements, and if we heat a specimen of any substance presented to us for analysis sufficiently to resolve it into its elements and to drive these into the state of vapour, then will the position of the bright lines of the spectrum of the flame obtained enable us to ascertain what elements were present in the substance, since each element will furnish its own peculiar lines, which are supposed to be known and recognizable. It was first remarked by Professor Swan that by means of the well-known and peculiar double line *D* the presence of a salt of sodium may be detected in a most delicate manner; and Bunsen and Kirchhoff, who have done much more than any one else to introduce and perfect this method of analysis, remark that by means of the spectroscope the presence of less than $\frac{1}{100,000,000}$ of a grain of sodium may probably be detected. Bunsen has also by this means discovered two new metals, namely *cæsium* and *rubidium*. Our countryman Crookes has discovered *thallium*, and Messrs. Reich and Richter *indium*, and other elements have since been discovered by the same means.

241. Before concluding this chapter we ought to allude to the beautiful discovery of Kirchhoff, by which it has been proved that substances with which we are here familiar exist also in the atmospheres of the sun and stars. It had been observed, first by Wollaston and after him by Fraunhofer, that the solar spectrum contains a number of dark lines, while it is in other respects a continuous spectrum, and the latter observer extended his remarks to the spectra of many

of the fixed stars. The origin of these lines for a long time remained a mystery, nor was this mystery diminished when it was found by Fraunhofer that a bright band corresponding in refrangibility to the double dark line *D* of the solar spectrum was produced by the light of a flame containing sodium. Sir D. Brewster was the first who prepared the way for the solution of this problem, by shewing that analogous (not identical) lines might be artificially produced by interposing a jar of nitrous acid gas in the path of a ray of light. The inference naturally drawn from this experiment was, that the lines of the solar spectrum do not denote rays originally wanting in the light of the sun, but are due to the absorption of his light by some substance interposed between the source of light and the spectator. It was doubtful, however, whether this stoppage of light occurred in the atmosphere of the sun or in that of our earth, until the matter was finally settled by Kirchhoff, not however before the true explanation had been divined by Sir G. Stokes.

Kirchhoff found that a sodium flame which gives out on its own account the double line *D* absorbs a ray of the same refrangibility when it is given out by a body of a higher temperature than the sodium flame, thus producing a dark line *D* instead of a bright one, and he therefore conjectured that the dark line *D* in the light of our luminary was occasioned by the presence of the vapour of sodium in the solar atmosphere, at a lower temperature than the source of light. This belief was strengthened by his finding that many of the dark solar lines correspond in position with the bright lines given out by metallic vapours, and by this means he detected the presence not only of sodium but also of iron, nickel, calcium, magnesium, barium, copper, and zinc, in the atmosphere of our luminary. In Fig. 60 we have a sketch of the appearance presented

when the sun's spectrum is compared with that of the vapour of sodium.

By a similar process Messrs. Huggins and Miller have detected the presence of various elements in Aldebaran and other stars.

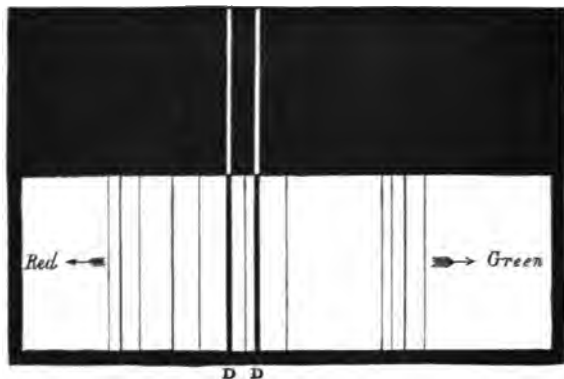


Fig. 6o.

More lately Mr. Huggins, in directing his spectroscope to certain nebulae, was surprised to find that their light resolved itself into bright lines with a dark background. The position of these lines appeared to indicate the existence in these curious bodies of incandescent hydrogen gas.

Still more recently Professor Donati in Italy, and Mr. Huggins in this country, have made observations which would appear to indicate that the physical constitution of comets is analogous to that of the nebulae above mentioned, and the latter observer finds that the light from the nucleus of a comet consists of bright lines, appearing thus to indicate ignited gas; while, on the other hand, the coma has apparently a continuous spectrum.

Again, M. Janssen the French observer, and Mr. Lockyer in this country, have found that the red flames which

are seen by the eye to surround the sun when he is totally eclipsed can be detected by means of the spectroscope on ordinary occasions. Mr. Lockyer finds by this means that an atmosphere consisting of hydrogen surrounds our luminary for about 5,000 or 6,000 miles above his apparent surface into which there are occasional injections of the vapours of sodium, magnesium, and iron.

One of these hydrogen lines in the sun's atmosphere was noticed by this last-named observer to present the appearance of an arrow head with its thickest part resting on the sun. This is a bright line corresponding in position to the dark line *H'*, and Dr. Frankland and Mr. Lockyer have found by laboratory experiments that the thickness of this line of hydrogen depends upon the pressure under which the gas exists, so that it is not improbable the spectroscope may ultimately give us the means of measuring the pressure and the temperature of the various strata of the atmosphere of our luminary.

The following statement will bring before the reader the most recent developments of this interesting subject.

It had already been observed by Kirchhoff that sometimes one or more of the spectral lines of an elementary vapour appeared to be reversed in the solar spectrum, while other lines did not experience reversal.

Mr. Lockyer has succeeded in obtaining certain results which throw much light on this phenomenon.

Hitherto, when taking the spectrum of the electric arc between two metallic terminals the arrangements were such as to give an average spectrum of the metal of these; if however we submit to the spectroscope a cross section of the arc midway between the poles we shall find that the central portion of this cross section is rich in lines while the borders give us comparatively few.

Thus there are many short lines which confine themselves

to the central portions, and a few long lines which extend all the way across.

We are thus led to regard the short lines as those which probably require a greater density or nearness of the vapour particles before they make their appearance; while on the other hand those which extend all the way across may be regarded as those which will continue to make their appearance in vapour of great tenuity.

Now it was remarked that these long lines were the very lines which were reversed in the atmosphere of the sun. Hence when we observe a single coincidence between a dark solar line and the bright line of any metal we are further led to inquire whether this bright line is one of the long lines which will continue to exist all the way across the arc of that metal. If this be the case, then we may argue with much probability that the metal in question occurs in the solar atmosphere; but if on the other hand, the coincidence is merely between a solar dark line and a short bright one, then we are led to imagine that it may not be a true coincidence, but something which will probably disappear on further examination.

Let us now imagine that we have terminals of some one metal which is however contaminated with a very slight admixture of some other metal. When we obtain the spectrum of the cross section of the arc as above described we shall obtain all the lines of the first metal but only the long lines of the second which exists in very small quantity as a contamination.

When therefore we find the spectrum as above taken of one metal giving us certain lines that are coincident with the long ones of some other metal we may imagine that the latter exists in the former as an impurity.

We are thus enabled to dispose of a good many cases of

alleged coincidence between the spectral lines of certain elementary metals, which it is extremely difficult to obtain pure, but nevertheless Mr. Lockyer is of opinion that this will not account for all the coincidences and approximate coincidences observed between elementary spectra, and he thinks that there is evidence that the elements are to some extent split up at a very high temperature.

Let us here endeavour to realise what would be the behaviour of the spectrum if the so-called elements were not capable of simplification, and also what would be its behaviour if they were, and then find with which of these two hypotheses the true behaviour of the spectrum agrees best.

If the elements were absolutely simple bodies, we might still expect that the molecule of vapour of an element would be at a low temperature more complex than at a high one, and would therefore give out a more complex spectrum. As however the temperature was made to rise we might expect ultimately to obtain a certain spectrum which would represent the simplest mode of vibration of that element, and which would thenceforward remain, however much higher the temperature should be made to mount.

And again we should have no reason for supposing that the lines of the ultimate spectrum of one element should coincide in position with those of the ultimate spectrum of another element.

If therefore we had a mixture of all the elements, and subjected this mixture to a very high temperature, the resulting spectrum, under the supposition that each element is really an element, would never be simpler than the combined spectrum of the various elements.

On the other hand, if the elements were really compounds of some one primordial atom, we might expect that a very high temperature would split up their atomic structure,

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and simplify their spectra, so that at an enormously high temperature a mixture of all the elements might nevertheless give us a very simple spectrum. We might likewise expect that different elements might split up into common constituents, so that at a very high temperature the spectra of these elements would have certain lines in common.

It is towards the larger masses of the universe, the sun and stars, that we must look to find a mixture of all kinds of matter at very high temperatures, and when we have a brilliant bluish-white star containing a large proportion of the more refrangible rays, we have every reason for supposing this star to be at a very high temperature.

Now such stars exhibit an extreme paucity in the black lines which appear in their spectra, in which there is hardly anything else than certain prominent lines seen in the spectra of hydrogen, calcium, magnesium and sodium. This undoubtedly tells in favour of the power of high temperature to split up the so-called elements.

Again, Mr. Lockyer has reason to believe that a paucity of lines is characteristic of the lower and hotter levels of our sun, just as it is of stars hotter than the sun.

Let us now ask whether the spectra of the various elements have or have not certain lines in common. We have already seen that there are certain lines in the spectra of each element which appear long and thick, and it has been found that while such a line is, for instance, exceedingly prominent in some one element, other elements appear to possess it only not so prominently. If this were all, it might be accounted for by traces of impurity, but Mr. Lockyer believes there are coincidences between the spectra of the various elements not of this nature. There are coincidences of lines which are not the prominent lines of any one spectrum, and they give no signs of that variability of

brightness that might be expected to characterise lines due to impurities¹.

Now these are the very lines that appear in the hottest regions of our sun. On the whole there is an amount of evidence in favour of the hypothesis that our chemical elements are in reality combinations, but it cannot yet be considered as finally established.

It would thus appear that through the laws of radiation we are likely to attain much information regarding the structure of the universe, both as regards the constitution and materials of celestial systems, and perhaps also as regards the internal structure of material molecules.

CHAPTER V.

Radiant Heat.—Further Remarks on Absorption.

242. It has already been stated (Art. 183) that the spectrum of a radiant body may be divided into two spectra, according to the effects which the rays produce. The first of these is the heating, and the second the luminous spectrum.

The absorptive behaviour of substances with regard to the different rays of the spectrum is exceedingly varied in character, and forms at the same time a subject well worthy of our study both from its theoretical and practical importance.

With regard to light, we know that the absorption of a substance for certain rays produces the colour of the

¹ Messrs. Liveing and Dewar have shewn by the application of great dispersive power that some at least of these are only approximate coincidences. This still leaves unexplained the fact that various elements exhibit lines which if not absolutely coincident are yet exceedingly close together.

substance, and sometimes enables us to determine its composition by means of its peculiarity of colour; and as we are now able to study the behaviour of a substance not only with respect to light but also with respect to dark heat of all kinds, it is quite clear that we shall soon both extend our knowledge of the relation which substances bear to various kinds of rays, and also add largely to our means of discriminating between different substances.

We shall now treat shortly of the behaviour of bodies with respect to dark heat and to light, reserving for another chapter their behaviour with regard to actinic rays.

ABSORPTION OF DARK HEAT BY DIFFERENT BODIES.

243. Delaroche was the first to shew that bodies exercised a selective absorption for dark rays, or sifted a stream of dark heat passing through them; and from this he argued that such heat consists of different kinds of rays mingled together, just as white light consists of a mixture of differently coloured rays; and these conclusions of Delaroche have been abundantly confirmed by the experiments of Melloni. The method of analysis adopted by Melloni will be seen from the table on the opposite page, although the heat is not strictly dark, being the rays from a Locatelli lamp.

244. If we refer to alum in the first column of this table we find that only 9 per cent. of the heat from the naked lamp passes through a screen of this material, while 90 per cent. of heat which has already passed through one screen of alum is capable of passing through a second. So in like manner, choosing sulphate of lime from the first column, we find that it only passes 14 per cent. of naked heat, but 54 per cent. of heat which has already passed through the same material. The same thing may be remarked for

Transmission of 100 incident rays.

Names of substances interposed ; thickness, unless mentioned, 2.6 millimètres.	Rays from lamp.	Rays from alum, thickness 2.6 millimètres.	Rays from sulphate of lime, thickness 2.6 millimètres.	Rays from chromate of potash, thickness 2.6 millimètres.	Rays from green glass, thickness 1.85 millimètres.	Rays from black glass, thickness 1.85 millimètres.
Rock salt	92	92	92	92	92	92
Fluor spar	78	90	91	88	90	91
Iceland spar	39	91	89	56	59	55
Glass, thickness 0.5 mm.	54	90	85	68	87	80
" " 8 mm.	34	90	82	47	56	45
Rock crystal	38	91	85	52	78	54
Acid chromate of potash	34	57	53	71	28	24
Sulphate of baryta	24	36	47	25	60	57
White agate	23	70	78	30	43	17
Feldspar	23	23	58	43	50	23
Yellow amber	21	65	61	20	13	8
Opaque black mica, thickness 0.9 mm.	20	0.4	12	16	38	43
Yellow agate	19	57	64	24	35	14
Aigue marine	19	60	57	26	20	21
Borate of soda	18	23	33	23	30	24
Green tourmaline	18	1	10	14	24	30
Common gum	18	61	52	12	6	4
Sulphate of lime	14	59	54	22	9	15
" " thickness 12 mm.	10	56	45	17	5	0.4
Carbonate of ammonia . .	12	44	34	11	6	5
Citric acid	11	88	52	16	3	2
Tartrate of potash and soda	11	85	60	15	2	1
Alum	9	90	47	15	0.5	0.3
Glass, white	40	90	83	50	67	55
" violet	34	76	72	42	56	47
" red	33	74	69	41	54	45
" orange	29	65	58	36	48	39
" apple green	25	3	20	22	25	50
" mineral green	23	1	15	19	52	58
" yellow	22	49	46	27	35	30
" blue	21	47	42	26	34	29
" opaque black	16	0.5	18	11	42	52
" indigo	12	27	26	14	20	17

chromate of potash, green glass, and black glass, so that all of these substances are capable of sifting heat in such a manner that a second plate will pass a greater proportion of the heat which has already passed through one plate of the same material than it will of naked heat.

We see occasionally, too, evidences of athermanous combinations in the above table, just as red and green glass together produce an opaque combination. Thus rays which have passed through alum will scarcely pass at all through black mica or black glass, through green tourmaline or green glass. It appears that in particular black glass and alum are antagonistic combinations, and the reason is supposed to be that alum is exceedingly opaque for all rays below the red and transparent for those above it, while black glass, on the other hand, is comparatively diathermanous for rays up to red, but opaque for those above it.

Thus we know in a general way that there are different varieties of dark heat, but how these are distributed in the spectrum, or what are the positions of the absorption bands produced by a screen which exhibits a selective absorption for dark heat, we are only now beginning to know from Captain Abney's photographic experiments and Professor Langley's experiments with the bolometer.

245. More lately Professor Tyndall has made some very interesting experiments on the absorption of bodies, but especially of gases for dark heat. These were made by means of a very delicate thermo-electric apparatus, and from them we learn that the absorptive power of the three permanent simple gases for dark heat is exceedingly small. He has also shewn that where aqueous vapour is present in the atmosphere on a day of average humidity its absorption is upwards of sixty times that of the air itself. We append the following table from Professor Tyndall's memoir on the subject, though later observations do not confirm it.

Comparative absorption of various gases, each of the pressure of 1 inch of mercury.

Air	1	Carbonic oxide	750
Oxygen	1	Nitric oxide	1590
Nitrogen	1	Nitrous oxide	1860
Hydrogen	1	Sulphide of hydrogen .	2100
Chlorine	60	Ammonia	7260
Bromine	160	Olefiant gas	7950
Hydrobromic acid . .	1005	Sulphurous acid . . .	8800

246. The results of this table are very remarkable, and Professor Tyndall deduces from it the fact that, for the heat experimented on, the absorption of the simple gases is much less than that of the compound ones. It would also appear that the same chemical change which renders chlorine and bromine more transparent to light renders them more opaque to obscure heat. Professor Tyndall has likewise shewn that the absorptive power of scents for dark heat is very strong, as also that of ozone. With regard to the action of vapours, he found that of bisulphide of carbon to be very small; and he also found that a solution of iodine in liquid bisulphide of carbon forms a medium which may be rendered perfectly opaque for light while it is very transparent for dark heat. Enclosing this substance in rock salt, so as to form a lens, he was enabled by this means to cut off the luminous rays from the electric light, while he condensed the dark rays so powerfully as to produce ignition in the focus of his fluid lens.

ABSORPTION OF LIGHT BY DIFFERENT BODIES.

247. It is a well-known fact that a coloured body, such as red glass, absorbs one kind of light more than another; but even when bodies are apparently of the same colour their power of absorbing certain rays of light may be very different. In order, therefore, to analyse completely the

relation of a substance to light, a pure spectrum must be formed by means of a narrow luminous slit lighted up by the sun or by the electric light, and the substance to be examined must be held in front of the slit;—in this way certain rays will either be entirely wanting in the spectrum or at least be partially stopped, being absorbed by the substance in front of the slit.

The following example will serve to shew that bodies very similar in colour have nevertheless a very different selective absorption for certain rays of light. Port wine and blood are two fluids somewhat similar in colour, but the former merely causes a general absorption of the more refrangible rays of the spectrum, while the latter produces two dark bands in the yellow and green. These bands were first observed by Hoppe. Sir G. Stokes has chosen this very example in order to shew the value of selective absorption for light as a discriminating test of the presence of certain substances. He remarks that the colouring matter of blood contains a large quantity of iron, and that it might therefore be supposed that the colour is due to some salt of iron, more especially as some salts of the peroxide of iron have a blood-red colour. But there is found to exist a strong general resemblance, or family likeness, between salts of the same metallic oxide as regards the character of their absorption. Now none of the salts of iron give absorptive lines at all similar to those of blood, and Sir G. Stokes remarks that the assemblage of the facts with which we are acquainted seems to shew that the colouring matter of blood is some complex compound of the five elements, oxygen, hydrogen, carbon, nitrogen, and iron. This example is sufficient to shew the great importance of absorption as an auxiliary in chemical analysis. But in examining the selective absorption of bodies it is not necessary to have a solution. Thus, for example, if a spectrum be thrown upon a screen of paper

painted with blood, the same dark bands are seen in the yellow and green as when the light is transmitted through a solution of blood. We thus see that the colour of a paper screen so painted is really caused by absorption, even although the paper is viewed by reflected light, and that it is not in reflexion that the preferential selection for certain rays is generally made. The light, in fact, which is irregularly reflected from such a surface of paper has first of all to pass through a film of blood, and it is in this passage that the selective absorption is accomplished which produces the red colour.

248. Metallic reflexion. There are, however, some very curious exceptions to this rule. Gold, for instance, reflects yellow light most abundantly, while a very thin leaf of gold transmits blue and green but absorbs yellow. Haidinger was the first to notice this fact in a general way, which he expressed by saying that the reflected and transmitted light from gold are complementary to each other. Sir G. Stokes was, however, the first to examine the subject in a complete manner. The substance he used was permanganate of potash. Crystals of this substance have a metallic appearance and reflect a greenish light. When this green reflected light is analysed by the prism, bright bands are observed, denoting a maximum of reflecting power; and these bright bands correspond in position to dark bands in the light transmitted by a solution of the same crystal.

This is an exceedingly remarkable phaenomenon, and it is the more interesting as it appears to be entirely confined to metallic and quasi-metallic bodies¹.

¹ Professor Magnus has made some very important experiments on the reflective power of substances for dark heat. He finds that fluor spar at an angle of 45° reflects from 6 to 10 per cent. of most kinds of heat, but of heat from rock salt it reflects from 28 to 30 per cent. On the other hand, heat derived from rock salt is almost completely absorbed by fluor spar.

It is thus rendered probable that this substance behaves towards the

There are yet other peculiarities exhibited by bodies in their action upon different rays, but these must be reserved until next chapter.

CERTAIN PRACTICAL CONSEQUENCES.

249. Suppose that we have a large heated globe, as in Fig. 61: and in the first place, let there be no envelope



Fig. 61.

round it, but let it be free to radiate its heat into space without receiving back any in return. Let its velocity of radiation be denoted by R . Suppose now that this sphere is closely surrounded by a very thin envelope, opaque as regards the heat from the sphere; and let us imagine that there is no heat conveyed from the sphere to the envelope either by convection or conduction,

or in any other way than by radiation. Now let R' denote the radiation of this envelope outwards into space, then R' will also approximately denote the radiation of the envelope inwards towards the sphere, since, as the envelope is very thin, both its surfaces may be imagined to be of the same temperature.

Hence the radiant heat which leaves the envelope will be $2R'$, while that which reaches it from the globe will be R .

But if the globe be very large, and cool very slowly, the envelope will, it is clear, settle down into a state of equi-

heat from rock salt in the same manner as permanganate of potash behaves towards green light.

brium of temperature, and therefore its absorption will be equal to its radiation ; that is to say,

$$R = 2R', \text{ or } R' = \frac{R}{2}.$$

We see, therefore, that by an arrangement of this nature the uncompensated radiation of the globe is diminished by one half, and by additional envelopes it would be still more diminished. The envelope has thus served to retain the heat of the globe by diminishing its uncompensated radiation into free space.

If we imagine the globe to be a body of comparatively low temperature, an envelope of a substance like glass will be sufficiently opaque for such heat to answer the purpose above indicated.

Let it be further supposed that the direct rays of the sun are the source of heat which keeps up the temperature of the globe. These rays, proceeding from a source of very high temperature, will pass through the glass envelope with great facility, so that while this envelope will diminish the radiation from the sphere it will yet allow most of the rays from the source of heat to reach the sphere. Now imagine the sphere to be the bulb of a thermometer, and surround this with a thin glass envelope with a vacuum between, and it will be easily seen that by this means, even without the aid of a burning lens, the bulb may be heated by the rays of the sun to a considerable extent.

If we now suppose the source of heat, that is to say the sun, to be withdrawn, it is evident that the globe will cool more slowly with the envelope than without it, so that we may imagine the effect of such an envelope to tend in the first place to increase the temperature of the globe while the sun is present, and in the next to diminish the velocity of cooling when he is absent. But this twofold action of

such an envelope in such a case will depend, it is evident, upon its being more opaque to heat of low than to heat of high temperature. Glass is one substance of this kind, but it has already been mentioned that this property is very common, so much so indeed that very few substances are transparent to heat of low temperature.

250. It has long been imagined that the earth's atmosphere is a body of this kind, and that while it stops a comparatively small portion of the sun's rays in their progress to the earth, it stops a very large portion of those which are given out from the surface of the earth.

That this is a property of our atmosphere has been rendered very probable by the experiments of Professor Tyndall upon the absorptive power of aqueous vapour for heat of low temperature, which he finds to be very great;—greater probably that we can suppose it to be for heat of high temperature, such as the sun's rays.

From the known presence of aqueous vapour in our atmosphere we may therefore infer that we are surrounded by an envelope which passes with comparative freedom the rays of the sun, while it absorbs most of the dark heat from the surface of the earth. Whatever we may suppose to be the whole effect both as regards radiation and convection of such an atmosphere during the day, there can be little doubt that during the night the absorptive nature of the atmosphere for dark heat diminishes the rate of cooling of the earth and thus perhaps serves to render it a fit habitation for living beings.

251. **Rapid refrigeration in central Asia and in the African desert.** Professor Tyndall has remarked the effect which an absence of aqueous vapour exerts upon the climate of certain portions of central Asia, and on that of the great African desert of Sahara. Owing to this absence the cooling of the earth after sunset is exceedingly rapid.

Accordingly in central Asia the nights are very cold, and the winters almost unendurable. In the African desert, again, during the day the air is intensely heated, owing perhaps amongst other causes to the absence of evaporation; but during the night the refrigeration is so rapid that ice may sometimes be produced.

252. Formation of Dew. These remarks lead naturally to the subject of Dew. For the true theory of this phenomenon we are indebted to Dr. Wells, a London physician, who published an account of his experiments in 1818. By these he ascertained the following laws:—

1. Dew is most copiously deposited under a clear sky ;
2. And with a calm state of the atmosphere.
3. It is most copiously deposited on those substances which have a clear view of the sky ;
4. And which are good radiators (thus a gilded thermometer is less liable to be covered with dew than one ungilt) ;
5. And which are placed close to the earth.
6. The deposition of dew is always accompanied with a lowering of temperature ; and at those places where dew falls most copiously the temperature sinks lowest.

Dr. Wells soon saw that the deposition of dew was owing to radiation. A solid substance which is a powerful radiator and is exposed to the clear sky gives off a great deal of its heat by uncompensated radiation into space, and is thus reduced below the temperature of the surrounding air. The particles of air in contact with the substance share in this reduction until they reach a temperature at which they can no longer retain their aqueous vapour, but must deposit it on the solid body.

We thus see why dew is most copious under a clear sky ; and if we reflect that the solid body is colder than the surrounding air, and can only obtain dew by cooling the

particles of air in contact with it, we see the necessity for calmness of atmosphere. We see also why the substance must have a clear view of the sky.

Since the deposition of dew is the effect of cooling, we see why it is always accompanied with a fall of temperature; and the hypothesis that the lowering of temperature is caused by radiation is also quite in accordance with those experiments in which Dr. Wells found that dew is most copiously deposited on good radiators.

It is not at first sight so obvious why a substance suspended a little above the earth should have less dew than one at the earth's surface; but Dr. Wells' explanation is no doubt the correct one; he remarks that, in the case of a substance above the earth, when the air in contact with it becomes cooled it also becomes heavier and sinks down, its place being supplied by lighter and warmer air. The cooling in this case, just as in that in which there is a horizontal movement of the air, is not sufficiently intense to produce dew.

253. Artificial formation of ice. Dr. Wells by means of this theory was able also to explain the formation of ice in Calcutta, where shallow pans containing water are during night exposed to the clear sky, and are often in the morning covered with a layer of ice.

Professor Tyndall has justly remarked that the formation of ice under these circumstances, while it is due to radiation, demands nevertheless an absence of aqueous vapour from the air; and he quotes in favour of this view the remark of Sir Robert Baker, who, speaking of the formation of ice in Bengal, says that the nights most favourable for its production are those which are clearest and most serene, *and in which very little dew appears after midnight.*

CHAPTER VI.

Radiant Heat.—Phosphorescence and Fluorescence.

254. Phosphorescence. In the preceding chapters it has been attempted to shew that the radiation of a heated body is, both in quantity and quality, dependent upon the temperature of the body, and on it alone; and this law may be regarded as a very accurate expression of a great number of facts. Accordingly, if a thermometer were raised to 100° Fahr., either by exposure to the direct rays of the sun, or by immersion in hot water, we should expect to find its radiation precisely the same in both cases, and we should be right in our expectation.

Nevertheless, there are certain substances in which the nature of the radiation depends not altogether on their present temperature, but to some extent upon the kind of rays to which they have recently been exposed ¹.

Such bodies are said to be *phosphorescent*. It has been shewn by E. Becquerel that the property of becoming phosphorescent belongs to a great number of substances. Thus, if we take a tube containing powdered sulphide of calcium, or sulphide of strontium, and expose it to sun light or to the electric light, if viewed afterwards in the dark it will remain luminous for several hours. Evidently this luminosity is not due to the temperature of the powder; and since this appearance takes place whether the powder be in vacuo or in air, it cannot be due to chemical action, and is probably rather due to a modification in the molecular state of the body caused by the action of light.

The same phaenomenon may be observed in many diamonds, in fluor spar, arragonite, chalk, heavy spar, and

¹ We have as yet been able to study this peculiar behaviour of bodies only with respect to those rays which are visible to the eye, and hence all this chapter treats of light.

a number of other minerals ; also among organic substances, in dry paper, silk, cane-sugar, &c.

255. In many instances this exhibition of light lasts for a considerable time after the exposure of the substance to the exciting source ; but in some cases it disappears in a few seconds, or even in a very small fraction of a second. In order to investigate the duration of this effect Becquerel has invented an instrument called a phosphoroscope. In this instrument two disks are placed parallel to one another on the same axle, and the substance to be tried for phosphorescence is placed on a fixed support between these disks ; there are apertures in these disks, but the aperture in the one is not opposite to that in the other, so that it is impossible to see through the disks. Suppose now that near that disk which is furthest from the eye there is a source of light, such as the sun or the electric light, and that the disks by means of a suitable train of wheels are made to revolve with great rapidity ; then at the time when the aperture of the disk furthest away exposes the phosphorescent substance in the support to the rays of light it will be hidden from the eye of the observer by the nearest disk, but a moment afterwards the opening of this disk will reveal it, and if phosphorescent it will then appear luminous. It is clear that by this arrangement the length of time elapsing between the exposure of the substance to the source of light and afterwards to the eye of the observer will depend upon the rapidity of rotation, and may therefore be made as small as possible. The observations must be made in a dark chamber. Becquerel found by this means that compounds of uranium are luminous only if viewed $\cdot 003$ or $\cdot 004$ of a second after exposure.

256. Fluorescence. Sir David Brewster was the first to remark that when the sun's light is condensed by a lens and admitted into certain solids or fluids, there appears

to be an internal dispersion of the rays. Some time afterwards, in 1845, Sir J. Herschel began to study a very curious phaenomenon connected with sulphate of quinine—which is in reality a colourless liquid—namely, that under certain aspects a solution of this substance exhibits a beautiful blue colour. This may be readily verified by viewing by daylight a solution of this substance placed in an ordinary test tube. Sir J. Herschel shewed that the incident light, after passing through a small thickness of the fluid, although not sensibly enfeebled or coloured, had lost its power of producing this effect. In a solution of quinine therefore there is a copious dispersion of light, which takes place near the surface, while there is also a feeble dispersion for a long distance within the fluid; and Sir D. Brewster was led to the belief that the dispersion produced by sulphate of quinine was only a particular case of internal dispersion. The phaenomenon is termed *fluorescence*.

257. Sir G. Stokes has since explained this phaenomenon with great success. The circumstance to which he directed his attention was the fact that a very thin stratum of the fluid is sufficient to deprive the light of the power of again producing the same effect. The rays producing dispersion, he was led to see, are very quickly absorbed; but he remarked that the dispersed rays themselves are able to travel many inches of the fluid with great freedom. The rays producing dispersion are therefore of a different nature from the dispersed rays.

Sir G. Stokes was thus led to recognize a change in the refrangibility of the rays when they become dispersed. If it further be supposed that the rays causing dispersion are the invisible rays beyond the violet, this will account for the circumstance that the visible appearance of the light is not changed when it is deprived of its power of producing this phaenomenon; and it will also account for the

fact that the blue appearance can hardly be seen by candle light, which is deficient in chemical rays beyond the violet.

258. In order to prove this change of refrangibility Sir G. Stokes instituted a very extensive series of experiments, from which he deduced the following results:—

1. In the phaenomenon of true internal dispersion the refrangibility of light is changed.

2. The refrangibility of the incident light is greater than that of the dispersed light to which it gives rise¹.

3. The nature and intensity of the light dispersed by a solution appear to be strictly independent of the state of polarization of the incident rays. The dispersed light is unpolarized, and appears to emanate equally in all directions, as if the fluid were self-luminous.

4. The phaenomenon is found to be extremely common, especially in the case of organic substances.

5. It furnishes a new chemical test of a remarkably searching character, which seems likely to be of great value in the separation of organic compounds.

Sir G. Stokes has given a list of highly sensitive substances, of which the following is an extract:—

Glass coloured by peroxide of uranium.

A solution in alcohol of the green colouring matter of leaves.

A weak solution of the bark of the horse-chestnut.

A weak solution of sulphate of quinine, namely a solution of the common disulphate in very weak sulphuric acid.

Certain varieties of fluor spar.

Red sea-weeds of various shades.

Various solutions obtained from archil and litmus.

Safflower red, scarlet cloth, and various other dyed articles in common use.

¹ Certain experiments by other observers would seem to indicate that this law is not universal.

259. It is important to notice the very striking likeness between the phaenomena of fluorescence and those of phosphorescence, noticed in the preceding part of this chapter: *in both cases it is found that the most refrangible rays of the spectrum produce the effect, and the dispersed rays appear nearly always to have a lower refrangibility than the rays producing dispersion.*

In fact, it is now generally believed that the only difference between the two phaenomena is one of *duration*, and that whereas in phosphorescence the acquired luminosity may last for a considerable time, in fluorescent substances, or at least in fluorescent solutions, the effect vanishes almost instantaneously when once the exciting ray is withdrawn.

260. In conclusion, it ought to be observed that the phaenomena of fluorescence and phosphorescence afford peculiar facilities for the study of the invisible rays of the spectrum beyond the violet, and also for the study of the effects of the rays on different substances.

In order to obtain all the information which these phaenomena can give, it is necessary to form the spectrum by means of a prism of rock crystal, and to use likewise a rock crystal lens, as this substance allows the more refrangible rays to pass, while they are absorbed by glass. If a spectrum so formed be thrown upon a screen, any substance to be examined for fluorescence or phosphorescence ought to be placed at the more refrangible end of the spectrum, and if it is found to become luminous in that position it may be assumed that it is fluorescent or phosphorescent.

If the object of the observer be to study the fixed lines in the invisible ultra violet portion of the spectrum, a screen of paper washed with a moderately strong solution of sulphate of quinine may be employed. The screen will thus be fluorescent, and will shine when exposed to the

invisible rays, except for that part of it which corresponds to a dark line. The position of the dark line is thus obtained, and by this means Sir G. Stokes has been able to represent the spectrum far beyond the violet. It is needless to mention that a spectrum so obtained will agree in the position of the dark lines with one obtained by any other process.

CHAPTER VII.

Conduction of Heat.

261. If one end of a poker be placed in the fire and allowed to remain there, the other end will in course of time become hot; the heat is thus conveyed to the further end of the poker by means of the particles of the poker itself, and this mode of conveyance is termed the conduction of heat.

Many simple experiments might be mentioned in illustration of this property possessed by bodies of conveying heat by means of their particles. Thus if a silver spoon be held in the flame of a candle or thrust into hot water, the end which is held in the hand will soon become inconveniently hot, while if a wooden or stone-ware spoon be used instead, no inconvenience will be felt by the hand, for in this case the particles have not the same facility for conducting heat.

We thus perceive a difference between the conducting power of different substances, and indeed it is well known that the faculty of conducting heat is possessed by metals much more than by other bodies; gems and hard stones come next in order; while certain organic substances, such

as wool, feathers, &c., and gases, such as air, possess the property to a very limited extent. Another familiar experiment is to wrap a handkerchief tightly round a polished ball of metal; this may be held for some time in the flame of a candle before the handkerchief is burned, the heat being conducted rapidly into the substance of the metal. If however the ball be of wood instead of metal, the handkerchief will very soon take fire.

262. Conduction of heat, it will at once be seen, is a very different thing from radiation; and yet there is this bond of union between the two, that they both tend to diffuse heat in such a manner as ultimately to produce equality of temperature. Thus it has already been stated (Art. 198) that a thermometer placed in an enclosure of constant temperature will ultimately attain the temperature of the enclosure, and it is no less true that in a pot of melted metal the thermometer will attain the temperature of the metal; a good conductor, therefore, such as a metal, distributes heat by conduction very rapidly, a bad conductor very slowly.

263. The conducting power of a body may be roughly recognized by the touch: thus if the temperature of a bar of metal be much higher than that of the hand, on touching it, heat is rapidly conveyed from the metal to the hand, and the sensation of heat is felt. Again, if the metal be much colder than the hand, heat is rapidly conveyed from the hand to the metal, and the sensation of cold is felt.

If, however, the substance be a very bad conductor, such as a woollen texture, we can handle it with impunity, even although it be considerably hotter or considerably colder than our body, and we can use it as clothing to protect us from the cold, since although the outer surface of such a texture may be exposed to a low temperature, yet the interior does not rapidly carry off the heat from our body;

such an envelope in such a case will depend, it is evident, upon its being more opaque to heat of low than to heat of high temperature. Glass is one substance of this kind, but it has already been mentioned that this property is very common, so much so indeed that very few substances are transparent to heat of low temperature.

250. It has long been imagined that the earth's atmosphere is a body of this kind, and that while it stops a comparatively small portion of the sun's rays in their progress to the earth, it stops a very large portion of those which are given out from the surface of the earth.

That this is a property of our atmosphere has been rendered very probable by the experiments of Professor Tyndall upon the absorptive power of aqueous vapour for heat of low temperature, which he finds to be very great;—greater probably that we can suppose it to be for heat of high temperature, such as the sun's rays.

From the known presence of aqueous vapour in our atmosphere we may therefore infer that we are surrounded by an envelope which passes with comparative freedom the rays of the sun, while it absorbs most of the dark heat from the surface of the earth. Whatever we may suppose to be the whole effect both as regards radiation and convection of such an atmosphere during the day, there can be little doubt that during the night the absorptive nature of the atmosphere for dark heat diminishes the rate of cooling of the earth and thus perhaps serves to render it a fit habitation for living beings.

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CHAPTER VI.

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Nevertheless, there are certain substances in which the nature of the radiation depends not altogether on their present temperature, but to some extent upon the kind of rays to which they have recently been exposed¹.

Such bodies are said to be *phosphorescent*. It has been shewn by E. Becquerel that the property of becoming phosphorescent belongs to a great number of substances. Thus, if we take a tube containing powdered sulphide of calcium, or sulphide of strontium, and expose it to sun light or to the electric light, if viewed afterwards in the dark it will remain luminous for several hours. Evidently this luminosity is not due to the temperature of the powder; and since this appearance takes place whether the powder be in vacuo or in air, it cannot be due to chemical action, and is probably rather due to a modification in the molecular state of the body caused by the action of light.

The same phaenomenon may be observed in many diamonds, in fluor spar, arragonite, chalk, heavy spar, and

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BG and GD represent the temperature difference and thickness of the wall, and hence—

Flow of heat varies as $\frac{BG}{GD}$, or varies as $\tan BDG$.

This law has been experimentally verified by M. Peclet.

270. Definition of conductivity. We are now in a position to define thermal conductivity. *Supposing that we have a wall an unit in thickness, then by the conductivity of this wall we mean the quantity of heat referred to some constant unit which passes in an unit of time across an unit of surface of such a wall, the difference of temperature between the two sides being an unit of our thermometric scale.* To make this still plainer, let us adopt as our unit of heat the quantity necessary to raise one kilogramme of water from 0°C to 1°C , and as our units of space, time, and temperature difference, let us adopt one mètre, one minute, and one degree centigrade; then will the conductivity of the wall be denoted in this case by the number of kilogrammes or fractional parts of a kilogramme of ice-cold water which will be raised in temperature one degree centigrade by the heat which passes in one minute across one square mètre of this wall one mètre thick, the difference of temperature between its two sides being one degree centigrade.

If the substance of the wall be changed, so that, while other conditions remain the same, twice as much heat passes across it in one minute, then we say that the second substance has twice the conductivity of the first.

Let C denote the conductivity of such a wall and F the flow of heat across unity of surface in unity of time: then if in Fig. 63 we denote our different units by equal lines, we have—

$$F = C \times \frac{BG}{GD} = C \times \tan BDG = C \times \text{rate of decrement of temperature.}$$

271. Flow of heat along a bar. It is not, however, by

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experiment the bar beyond the point of immersion must be defended by means of screens (Fig. 65) from the influence of the source of heat, so that the bar beyond *A* may be heated by conduction of heat, and by nothing else.

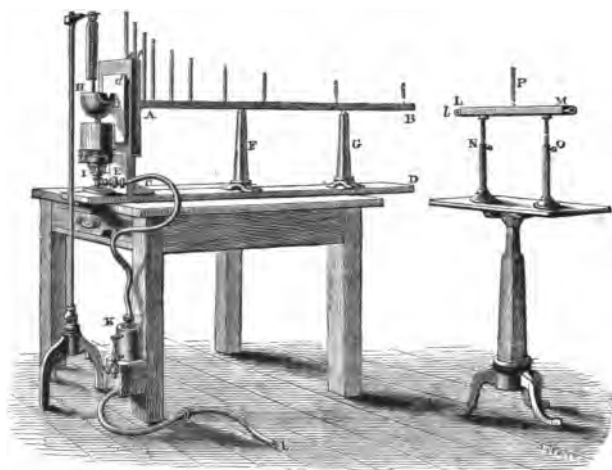


Fig. 65.

By means of thermometers plunged into small holes drilled in the bar, and kept by some fluid metal in metallic contact with the bar itself, the temperature of each part of the bar was accurately ascertained. An auxiliary bar *LM*, hung in the room sufficiently far from the source of heat, served to determine the temperature of the room. Subtracting this from the temperature of the various parts of the bar *AB*, the difference will represent the excess of temperature of each part of *AB* due to the source of heat at *A*, and by having a sufficient number of thermometers a curve of temperature *DE* may be obtained, of which the ordinate *AD* represents the excess of temperature at *A*, the ordinate *CF* the excess at *C*, and so on. At the point *E*,

where this curve cuts the bar, there is no excess of temperature; that is to say, E and all points beyond it are virtually unaffected by the source of heat at A .

272. Now it is clear that heat is constantly flowing outwards across any section CC' of the bar, but since by hypothesis all parts of this bar have attained a constant state with respect to temperature, the flow of heat across CC' does not increase the temperature of the bar beyond CC' ; what then does it do? A little consideration will shew that it is all spent in radiation and convection of hot air from the heated surface of the bar beyond CC' .

If, therefore, we are able to estimate the value of this radiation and convection for each portion of the bar beyond CC' , the integral of this effect will represent the flow of heat across CC' , which, as we have just now seen, is entirely carried off by radiation and convection.

273. Suppose that by this means we have been able to ascertain the flow of heat across CC' . Now let cc' represent another cross section of the bar a little (but very little) farther off than CC' from the source of heat, and let CF denote the temperature of the first section, and cf that of the second, the difference between these two temperatures is therefore ϕF , while the distance between the two sections is ϕf ; our units of temperature and length being denoted by equal lines.

Hence if we imagine the sectional area of the bar to be denoted by unity, according to Art. 270, we shall have—

$$\text{Flow of heat across } CC' = \text{conductivity} \times \frac{\phi F}{\phi f} = \text{conduc-}$$

tivity $\times \tan Ff\phi = \text{conductivity} \times \text{tangent of the angle denoting the downward slope of the temperature curve at the point } F;$

and hence

$$\text{conductivity} = \frac{\text{flow of heat across } CC'}{\tan Ff\phi} \quad (1)$$

274. In this experimental investigation it is therefore necessary to determine two things: in the first place, we must have the means of drawing a true temperature curve; and secondly, we must be able to estimate the whole loss of heat, due to radiation and convection united, beyond any section CC' , since this, as we have seen (Art. 272), will represent the flow of heat outwards across the same section.

We have already stated how, in this investigation, the curve of temperature was determined by means of thermometers plunged into small holes in the bar, and we shall now proceed to shew how the amount of heat carried off by radiation and convection united beyond any given cross section CC' was determined. For this purpose a smaller but otherwise similar bar LM (Fig. 65) was heated to a temperature at least equal to the highest temperature of the bar AB . A thermometer P plunged into a small hole in the centre of this bar gave the velocity of cooling at the various temperatures of the bar.

It is clear from what we have already said (Arts. 228, 229) that the velocity of cooling of such a bar really denotes the rate at which heat is momentarily carried off by radiation and convection united from the bar at the various temperatures of observation, and a little reflection will convince us that by making use of these observed velocities of cooling we may be able to estimate the amount of heat carried off momentarily from all portions of the similar bar AB by radiation and convection united, since we know by the curve we have drawn the temperatures of the various parts of this bar.

Having thus estimated the amount of heat carried off by convection and radiation united from the surface of the bar AB past any cross section CC' , we can find at once its equivalent or the flow of heat across this same section.

Knowing therefore this flow of heat, and being able to determine by means of the curve of temperatures the tangent of the angle denoting the downward slope of the temperature curve at any point F , we are able at once from the expression (1) Art. 273 to determine the conductivity at any section CC .

275. It will be observed that this process is entirely devoid of any theoretical assumption with regard to the laws of radiation and convection, and that it may even be employed for the purpose of finding whether the conductivity of the bar AB varies from one point to another, or whether it is constant throughout. If this be constant throughout, then the expressions for the conductivity found by the process above described for two different sections CC , GG' will be the same. On the other hand, if the conductivity be not constant, but vary with the temperature, then the expression found for one cross section CC will be different from that found for another section GG' , since the temperatures of these two sections are different.

276. It was mainly with the view of ascertaining whether the thermal conductivity of wrought iron varies with the temperature that Principal Forbes made these experiments, and the results obtained by him will be stated in a future paragraph. In the meantime, let us state the results obtained by other observers for the comparative thermal conductivity of the various metals.

M. Despretz was one of the first to make experiments on the subject, his instrument of research being a bar with thermometers plunged into it at different intervals from the source of heat. After him MM. Wiedemann and Franz investigated very carefully the relative conductivity of several of the most important metals. They operated with thin bars, and the temperature of these bars at the

various points was ascertained by means of a thermo-electric arrangement.

Their results are embodied in the following table.

Metal.	Relative Thermal Conductivity obtained from experiments.	
	in air.	in vacuo.
Silver	100.0	100.0
Copper	73.6	74.8
Gold	53.2	54.8
Brass	23.6	24.0
Tin	14.5	15.4
Iron	11.9	10.1
Steel	11.6	10.3
Lead	8.5	7.9
Platinum	8.4	9.4
Palladium	6.3	7.3
Bismuth	1.8	

We are probably furnished in this table with very good determinations of the relative conductivity of these different metals. The same remark ought however to be made here that was made on a former occasion, when a table of the linear dilatations of different metals was given, namely, that difference in quality makes probably a very considerable difference in conductivity; and there is reason to think that the relative conductivity of pure copper is considerably greater than that here given. This table gives however only the *relative* conductivity, and to complete our information we require to know the *absolute* conductivity of some one metal. One or two observations of absolute conductivity have been made. M. Peclet has determined the absolute conductivity of lead by finding how much heat was conveyed across a plate of this substance whose two sides were kept at unequal temperatures.

Principal Forbes, in connexion with the experiments already described, has likewise determined the absolute con-

ductivity of wrought iron. In his experiments conductivity was expressed in terms of the amount of heat as unity which is required to raise the temperature of one cubic foot of water by one degree centigrade. He expresses the amount of heat reckoned in such units which would travel in one minute across an area of one square foot a plate of iron one foot thick with the two surfaces maintained at temperatures differing by 1° centigrade. According to these experiments, the conductivity at 0° centigrade of one of his bars was $\cdot 01337$, while that of another bar was only $\cdot 00992$. This discordance was probably due to a difference in the quality of the iron of the two bars.

277. Variation of thermal conductivity with temperature. We have already mentioned that the main object of Principal Forbes in his research was to ascertain if the conductivity of an iron bar varies with its temperature. The method employed has already been described; it only now remains to mention the results. There were two square bars; the side of one being $1\frac{1}{4}$ in., while that of the other was 1 in.

The following table exhibits the thermal conductivity of these bars at the various temperatures of experiment.

Temperature Cent.	Conductivity (units, foot—minute—degree).	
	$1\frac{1}{4}$ in. bar.	1 in. bar.
0	$\cdot 01337$	$\cdot 00992$
25	$\cdot 01235$	$\cdot 00943$
50	$\cdot 01144$	$\cdot 00904$
75	$\cdot 01070$	$\cdot 00865$
100	$\cdot 01012$	$\cdot 00835$
125	$\cdot 00966$	$\cdot 00813$
150	$\cdot 00934$	$\cdot 00795$
175	$\cdot 00904$	$\cdot 00779$
200	$\cdot 00876$	$\cdot 00764$
225	$\cdot 00851$	$\cdot 00749$
250	$\cdot 00826$	$\cdot 00736$
275	$\cdot 00801$	$\cdot 00724$

It thus appears that in each case the conductivity diminishes as the temperature increases, the percentage decrement of conductivity between 0° and 100°C being 24.5 for the large and 15.9 for the small bar of iron.

278. Similarity of bodies as regards their thermal and electric conductivity. Forbes was the first to shew that metals follow each other in the same order as conductors whether of heat or of electricity.

The following table, confirming this remark, was drawn up by MM. Wiedemann and Franz when they were engaged in determining the thermal conductivity of metals.

Names of metals.	Electric conductivity.			Thermal conductivity.
	Riess.	Becquerel.	Lenz.	
Silver	100.0	100.0	100.0	100.0
Copper	66.7	91.5	73.3	73.6
Gold	59.0	64.9	58.5	53.2
Brass	18.4	...	21.5	23.6
Tin	10.0	14.0	22.6	14.5
Iron	12.0	12.35	13.0	11.9
Lead	7.0	8.27	10.7	8.5
Platinum	10.5	7.93	10.3	6.4
German Silver	5.9	...	...	6.3
Bismuth	...	...	1.9	1.8

This similarity between bodies as regards their thermal and electric conductivities does not extend except in the case of iron to the decrement which their conductivity suffers when their temperature is increased.

In Art. 168 the decrement of the electric conductivity of iron between 0° and 100°C as determined by Matthiessen and Von Bose was found to be 38.26 per cent., while for the same metal and between the same limits of temperature Forbes, as we have just seen, has found a decrement of 24.5 and 15.9 per cent. in the thermal conductivity of his iron

bars. The numerical value of the decrement for heat is thus considerably smaller than that obtained by Matthiessen for electricity.

In 1878 Professor Tait continued Forbes' experiments and obtained the following remarkable results.

1. The thermal conductivity of iron diminishes as its temperature is raised.

2. At temperatures above 150°C the diminution of conductivity of iron is less rapid than that assigned by Forbes. The conductivity seems to reach a minimum somewhere about red-heat.

3. The thermal conductivity of copper and lead changes much less than that of iron with rise of temperature, and probably in the sense of increase instead of diminution. The same is true of German silver.

4. Electrically bad copper conducts heat worse than electrically good copper, but not in the same ratio.

5. The metals examined have the same order as conductors of heat and of electricity. The alloy (German silver) violates this arrangement.

279. Difference between transmission of heat and transmission of temperature. If the definition of thermal conductivity be considered, it will be found that it takes account of the quantity of heat referred to some unit which passes across a substance in unit of time.

Suppose now that we have two bars of different substances, but of precisely the same conductivity, and also of the same shape and surface covering, and that we heat the ends of both to the same extent. If we allow a sufficiently long time to elapse, we shall no doubt find the distribution of temperature in both bars to be the same. But if we examine them both at the end of a short time, such as a minute, it does not follow that at the distance, say, of one inch from the heated end, they will both have the

same temperature. The two cases are very different. In the former, the bar has attained a permanent temperature condition, and the flow of heat outwards is entirely spent in radiation and convection. If therefore two such bars of equal conductivity be coated with the same substance, so that their external surface is the same, then both bars will be similarly affected by radiation and convection. Referring therefore to previous articles, there is evidently no reason why any of the elements should be different in the two bars. Both will therefore have the same curve of temperature.

But in the second case, when we allow only a minute to elapse, the state of things is very different. Here the particles of the bar are in the act of rising in temperature; a great portion of the flow of heat is therefore spent in increasing the temperature of the bar. Now it may take much more heat to raise a given slice of the one bar one degree in temperature than it will take to raise a similar portion of the other.

The following experiment in illustration of this has been made by Professor Tyndall. Take two precisely similar prisms, one of bismuth and one of iron, and coat the ends of each with white wax, and place them with their coated ends upwards on the lid of a hot vessel. The wax will first melt on the bismuth, although by the table of Art. 278 it will be seen that iron is the best conductor. The reason of this is, that it requires more heat to raise the iron one degree in temperature than it does to raise the bismuth.

280. Safety-lamp. The present is perhaps the best opportunity of alluding to the safety-lamp, the action of which depends to a great extent on the withdrawal of heat by wire gauze.

If a surface of wire gauze be lowered into the flame of

a jet of gas, it will seem to crush the flame down, before it so that none will appear above. But if while the gauze is held in this position the flame be extinguished, and then the gas ignited above the gauze, in this case there will be no flame below. It would thus appear that the flame cannot pass through the gauze; and the reason is that the heat of the flame is transferred in a great measure to the mass of metal which is placed upon it, by which means the temperature is so much lowered that combustion is stopped.

An ingenious and useful application of this principle was devised by Sir Humphry Davy. He found by experiment that a lamp surrounded by wire gauze might burn in an atmosphere of explosive gas without communicating sufficient heat through the meshes of the gauze to produce explosion, so that a miner furnished with a lamp of this kind, and using it with proper care, will be secure from the action of fire-damp.

Quite recently it has been shewn by Mr. Galloway that a violent external explosion destroys the action of the safety-lamp and forces the flame to pass through the gauze.

CONDUCTIVITY OF NON-HOMOGENEOUS SOLIDS AND OF CRYSTALS.

281. Owing to their want of continuity, powders and tissues, such as wool, fur, feathers, &c., are very bad conductors of heat. The heat has in its course to pass so often from the substance into the air, and from the air back again into the substance, that its progress is extremely slow.

In substances which possess a fibre, the conducting power for heat in a direction across the fibre is generally different from what it is in the direction of the fibre.

MM. De la Rive and De Candolle were the first to remark

this property in the case of wood, in which they found that the conductivity was greater along the fibre than across it, and this result has been confirmed by Professor Tyndall. It has also been found by MM. Svanberg and Matteucci that bismuth conducts both heat and electricity better along the planes of cleavage than across them.

We are chiefly indebted to De Senarmont for our knowledge of the conduction of heat in crystals. He cut thin slices in different directions out of crystals, and piercing their thickness by small holes in the centre, he passed a wire through them along which a constant electric current was made to pass: the wire thus became very hot, and the heat was conducted on all sides of the hole. The slice of crystal was coated with wax, and the result of the heating of the crystal by means of the wire was a general melting of the wax all round the wire. If the substance was of equal conductivity in all directions then the wax melted in a circle, but if the conductivity was unequal it melted in an ellipse. The border of the melted portion represented by this method an isothermal line or curve possessing the same temperature throughout, this temperature being that of melting wax. De Senarmont thus determined that in quartz and calc-spar the axis of symmetry is the direction of greatest conductivity, while for a plate cut in a plane perpendicular to the axis of symmetry the conductivity is equal in all directions. A crystal of idocrase, however, conducts best at right angles to its axis.

De Senarmont has obtained the following laws:—

1. *If we could imagine a crystal of the first system, such as rock salt or fluor spar, to be heated at a point in its centre, the isothermal surface would be a sphere, or the conductivity will be equal in all directions.*
2. *If the crystal be of the second or third system, (symmetrical around one axis,) then the isothermal surfaces of such*

a crystal, heated internally at a point, would be spheroids, the axis being in the direction of the axis of symmetry.

3. *But if the crystal be of the system characterised by three unequal axes, then the isothermal surfaces are ellipsoids with three unequal axes.*

CONDUCTIVITY OF FLUIDS.

282. The conductivity of liquids may be determined in the following manner. In Fig. 66 let there be a vessel of water in which we place a differential thermometer, one bulb being near the surface and one near the bottom. Now place a vessel containing boiling water or boiling oil on the surface, and it will be found that the heat from this vessel will penetrate downwards very slowly, so that for a long time the differential thermometer will scarcely be affected. Water is thus proved to be a very bad conductor of heat. If we wish to try mercury, let the vessel of Fig. 13 be filled with mercury, and let a little alcohol on the surface be set on fire. It will be found that the thermometer will soon begin to rise, thereby shewing that mercury is a much better conductor than water.



Fig. 66.

Professor Guthrie endeavoured in 1869 to determine the thermal resistance of various liquids. The essential part of his apparatus consisted of two hollow cones, the first of which was erect and the second inverted so that the bases of the two might be brought together. In his experiments a film of the liquid to be examined was made to lie between these bases, its upper surface being in contact with the base of the first cone and its under surface with that of the

second. The cones were of brass, but their bases consisted of perfectly flat sheets of platinum. A current of hot water of known temperature was carried through the first or upper cone, while, on the other hand, the second or under cone was used as an air thermometer.

The experiment was performed in the following manner. In the first place the two cones were brought into actual contact, and the effect upon the lower cone or air thermometer of the heating agent introduced into the upper cone was noted. Other things remaining the same a liquid film of known thickness was then introduced between the two cones, and the effect upon the under cone or air thermometer noted as before—the difference between the two effects was taken as a measure of the thermal resistance of the liquid. By such means, using liquid films 1 millimètre in thickness and a temperature difference of 10°C , the following results were obtained.

Specific thermal resistance.		Specific thermal resistance.	
Water	1.0	Amylic alcohol . .	10.23
Glycerine	3.84	Oil of turpentine .	11.75
Acetic acid (glacial)	8.38	Chloroform	12.10
Sperm oil	8.85	Bichloride of carbon	12.92
Alcohol	9.09	Mercury amyl . . .	12.92
Nitrobenzol . . .	9.86	Iodide of amyl . .	13.27
Butylic alcohol . .	10.00		

In the next chapter it will be shewn that in liquids heat is communicated more by convection than by conduction. It is believed that the conductivity of gases is, like that of liquids, extremely small ; but this is a subject of which little is known experimentally, the difficulties being very great.

CHAPTER VIII.

Convection of Heat.

CONVECTION IN LIQUIDS.

283. It was stated in the last chapter that liquids, such as water, are very bad conductors of heat, and an experiment was described in which a vessel of water was heated on the upper surface—the effect travelling downwards very slowly.

The heating of the water would however have been greatly hastened if the vessel had been heated from below instead of at the top, and the difference between the result in the two cases is due to a process termed Convection, which we shall now describe. As the lower strata of water in such a vessel become heated the particles expand, and thus become specifically lighter than those above them. Consequently they rise

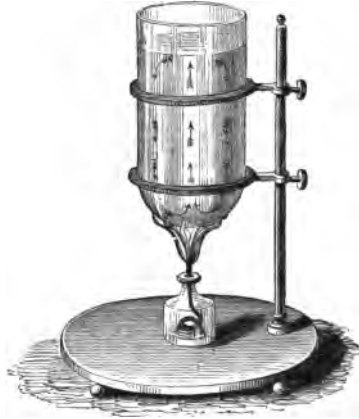


Fig. 67.

to the top, and are replaced by colder particles descending from above, for the same reason that a cork rises to the surface of the water, or a balloon rises in the air. By introducing a little colouring matter, such as fragments of cochineal, the course of these currents may be observed, and it will be found that there is a central current ascending from below and side currents descending from above, after the manner

of Fig. 67. In the Geysers of Iceland, which are large tubes of water heated from below, we have a natural instance of convection on a very large scale; and travellers relate that a small piece of paper thrown into the centre of the pipe is drawn to the side, and thence carried downwards by the descending current.

Another very good instance of the operation of convection is that described in Article 99, from which we see that the surface particles of a lake cooled at the top become specifically heavier, and descend until the whole body of water has attained the temperature $39^{\circ}\cdot2$ Fahrenheit, this being the point of maximum density of water. When the whole lake has attained this temperature the process of convection is at an end; and if the surface particles be cooled still further, they become lighter, not heavier; and instead of descending, remain at the top.

284. It will thus be observed that convection depends upon two things. In the first place, it depends upon the extent to which the liquid expands under heat; thus, for instance, if a body hardly expanded at all its convection would be very feeble. In the second place, convection depends upon the force of gravity. Were there no gravity there would be no convection; indeed the very term *specifically heavier* has a reference to gravity: so that if this force did not exist the effect of the heating would always be the same whatever was the part of the vessel to which the heat was applied.

CONVECTION IN GASES.

285. Convection takes place in air and gases even more energetically than in fluids, the coefficient of expansion of a gas on account of heat being comparatively great. Many familiar instances might be mentioned in illustration of the convection of air: thus, the air heated by a fire, being

lighter than that around it, rises upwards, sometimes carrying with it small particles of solid matter, which become visible in the form of smoke. Even where there is no opaque matter mixed with the air, the currents which form convection are rendered visible in another way. As air expands, its index of refraction becomes less, and the result of this is an apparent unsteadiness and indistinctness in objects viewed through heated air, which may be noticed above a lime-kiln, or in the air near the ground on a very hot day.

286. Trade winds, &c. In nature we have convection of air on a very large scale. The air of the equatorial zone expands under the powerful influence of a vertical sun, and, becoming lighter, ascends, while its place is supplied by cold air from the regions north and south of the equator. Let us confine our attention to the northern hemisphere, and consider the air which rushes south to supply the place of the air carried upwards in the equatorial regions.

The earth, it is well known, revolves from west to east: the body of air therefore which approaches the equator from the north comes from a place of smaller to a place of greater velocity of rotation and therefore lags behind, or in other words, appears to go towards the west; this current of air will therefore not blow directly from the north, but will rather be a current from the north-east. In like manner the cold air from the southern hemisphere blowing towards the equator will form a current from the south-east. These two currents blowing towards the equator in the two hemispheres are called the two *Trade Winds*.

Having thus considered the cold winds which come to replace the air carried upwards at the equator, let us now endeavour to trace the course of this equatorial air. When it has mounted to the upper regions of the atmosphere it proceeds northwards and southwards towards the poles; and

going from a region of greater to a region of less velocity of rotation, it gains upon the earth, or in other words, goes eastward. Could we ascend into the upper regions of the atmosphere at the equator, we should there find currents blowing from the south-west in the northern hemisphere, and from the north-west in the southern. These winds are called the *Return-Trades*, their direction being opposite to that of the trade winds.

At the equator this return current is very high, so that even the summits of the Andes are probably beneath it. Volcanic explosions have however sometimes occurred in these regions with sufficient force to drive ashes up into the return current, which, when they regained the earth at a considerable distance off, told by the course they had taken the direction in which the upper strata of air were moving.

As the return current proceeds north it gradually descends. At Teneriffe it has already fallen below the summit of the mountain, and it reaches the earth at about our own latitude; so that the south-west wind is perhaps more prevalent than any other in the British Isles: on the other hand, we are also often exposed to the trade wind in the form of a cold wind blowing from the north-east.

The land and sea breezes are probably produced by similar causes. During the day the land is more heated than the sea, and a vertical current is produced, carrying upwards the land air, which is replaced by air from the sea—this is the *sea breeze*. But after sunset the land cools more rapidly than the sea, and the cooled, and therefore heavier, land air moves seawards, thus producing the *land breeze*.

Bearing in mind what has now been stated, it is natural to suppose that convection currents should be very powerful in the atmosphere of our luminary. For, in the first place, the changes of temperature occurring there are no doubt

very great, in the second place the force of gravity is very intense, and lastly the expansion of gas through heat is very great. It is not therefore surprising that Mr. Lockyer should have observed on the solar disk traces of motions exceeding one hundred miles per second.

287. Law of cooling due to a gas. It has been already shewn (Art. 228) that a body placed in vacuo and surrounded by an enclosure of lower temperature than itself will gradually lose heat. If the body be surrounded not by a vacuum but by gas, it will lose heat more rapidly than in vacuo, and the difference between its velocity of cooling in the two cases is due to the presence of the gas. Thus the whole velocity of cooling of a body in air or gas is due partly to radiation and partly to the gas, but it is only the latter cause with which we are at present concerned. The velocity of cooling due to gas, or, which is the same thing, the amount of heat carried off momentarily from a body by gas, was investigated by MM. Dulong and Petit at the time when they also ascertained the law of cooling in vacuo.

This research was very troublesome; for the temperature of the thermometer, and the density, temperature, and chemical nature of the gas, had all to be varied before the exact law could be ascertained. The following results were obtained by these experimenters.

1. *The velocity of cooling due to the sole contact of a gas is entirely independent of the nature of the surface of the body.* Sir J. Leslie was probably the first to make this remark in a general way, and the truth of his remark has been well confirmed by the accurate experiments we are now describing. Thus, as far as gas or air is concerned, a silvered thermometer will cool just as rapidly as a blackened one; but as far as radiation is concerned, it will cool less rapidly than a blackened one.

2. *The velocity of cooling due solely to the contact of a gas is*

proportional to the excess of temperature in degrees C raised to the power 1.233. From this law also we see the difference between cooling in vacuo and the cooling due to a gas. In vacuo the effect for the same excess of temperature of the thermometer above the enclosure varies with the actual temperature of the enclosure (Art. 231), whereas in the case of a gas the effect depends only on the excess of temperature.

3. *The cooling power of a given gas and for a given excess of temperature depends not on the DENSITY but on the PRESSURE of the gas.* The following expressions give the relation between the velocity of cooling and the pressure (p) for the different gases, the excess of temperature being supposed constant throughout:—

For atmospheric air	the velocity of cooling	varies as	$p^{.45}$,
for hydrogen			$p^{.38}$,
for carbonic acid			$p^{.517}$,
for olefiant gas			$p^{.501}$.

Combining these three laws we have the following expression for the velocity of cooling due to a gas—

$$\text{Velocity of cooling in gas} = np^{\alpha}t^{1.233};$$

where n is a constant, depending partly on the dimensions of the body and partly on the nature of the gas; p is the pressure expressed in millimètres; α is an index which we have given above for four different gases; and t is the excess of temperature in centigrade degrees.

In order to express the cooling power of a gas in absolute units we must refer once more to a research of Mr. Hopkins already quoted (Art. 235). Let C denote the quantity of heat which would be carried off by a gas in one minute from a square foot of *any kind of surface* at t degrees C above the surrounding gas, of which the pressure, expressed in milli-

mètres, is p , the unit of heat being that amount of heat which would raise the temperature of 1000 grains of distilled water 1°C ; then

$$C = .0372 \left(\frac{p}{720} \right)^{.45} t^{1.233} \text{ for atmospheric air.}$$

Combining this determination with the researches of Dulong and Petit, and writing generally

$$C = \nu p^a t^{1.233},$$

we have for ν in Hopkins' units the values given in the third column of the subjoined table, the numbers in the fourth column being the corresponding values of ν when C represents the heat carried off in one second from one square centimètre, the unit of heat being that required to raise one gramme of water through 1°C .

Gas.	a .	Values of ν .	
Atmospheric air . .	.45	.001926	2.239×10^{-8}
Hydrogen . . .	.38	.010571	12.289 "
Carbonic acid . .	.517	.001196	1.391 "
Olefant gas . . .	.501	.001840	2.139 "

Example. Let it be required to find the *whole amount of heat due to convection and radiation united* which leaves a square foot of surface of dry chalk in one minute, the temperature being 50°C , while that of the surrounding enclosure is 14°C ; the enclosure being filled with hydrogen of the pressure of 760 millimètres. By reference to Art. 235 we find the whole expression for loss of heat in this case to be

$$\begin{aligned} V &= R + C \\ &= 8.613 \times 1.0077^{14} \times (1.0077^{36} - 1) + .010571 \times 760^{.38} \times 36^{1.233} \\ &= 3.050 + 10.908 = 13.958. \end{aligned}$$

It ought however to be borne in mind that all these formulæ are to a great extent empirical, representing the

experiments made, and useful only in so far as they enable us to calculate approximately the loss of heat due to radiation and convection in any case in which all the particulars are given.

Of late the word *emissivity* has been employed to denote the total loss of heat, by radiation and convection together, in one second by one square centimetre of surface per degree C of excess of temperature of the surface above the enclosure, the unit of heat being that amount which is required to raise one gramme of water from 0° to 1°C ; so that, the emissivity being e , the heat lost by an area of ω square centimetres in τ seconds for an excess t degrees C of temperature when the enclosure has temperature $\theta^{\circ}\text{C}$, is $e\omega\tau t$ units. Very extensive experiments have recently been made by several observers to determine the emissivity of copper in the form of balls and of platinum in the form of wires, with their surfaces both bright and blackened, and in air of different pressures. Prof. Ayrton and Mr. Kilgour have confirmed a conclusion of M. Péclet that in air at ordinary pressure the emissivity of a wire is of the form $a + b/d$, where d is the diameter and a, b coefficients, but have further shewn that these coefficients, as also their ratio b/a , increase with the temperature, so that the effect on the emissivity of fineness in the wire increases markedly with the temperature. For bright platinum wires in air at ordinary pressure they give the following values.

Diameter.	Emissivity at temperature		
	100°C.	200°C.	300°C.
mm.			
·0305	·01085	·01278	·01440
·0737	·00455	·00538	·00584
·1524	·00293	·00346	·00384
·2362	·00230	·00259	·00284
·3556	·00189	·00214	·00229

With a sooted copper ball, of 4 centimètres diameter, at about 114°C Dr. Bottomley found 3.42×10^{-4} for the emissivity in air at ordinary pressure and 1.40×10^{-4} for the emissivity in vacuo; and with the copper surface silvered and brightly polished the emissivities in ordinary air and in vacuo were 2.30×10^{-4} and 0.18×10^{-4} respectively at about 194°C . It seems likely however, from a comparison of the results of different experimenters, that the shape and dimensions of the enclosure have a marked effect upon the emissivity.

CHAPTER IX.

Specific Heat.

288. In order to arrive at a complete knowledge of the laws which regulate the distribution of heat through space, we must be able to measure the amount of heat which a body absorbs, or parts with, when its temperature is changed to a given extent, and also when it changes its state. To do this it is necessary to adopt some unit of heat, and we shall use in this work as our thermal unit the quantity of heat necessary to raise one kilogramme of water from 0° to 1°C .

In the present chapter we shall treat of the amount of heat which a body absorbs, or gives out, when its temperature rises or falls to a given extent. This is called *specific heat*, and we define the specific heat of a given substance to be the quantity of heat necessary to raise one kilogramme of the substance 1°C in terms of that necessary to raise one kilogramme of ice-cold water 1°C reckoned as unity. Thus, if a kilogramme of any substance required as much heat to raise it from 100° to 101°C as would raise three-tenths of

a kilogramme of water from 0° to 1°C , then we should say that the specific heat of this substance at this temperature was 0.3.

METHODS OF MEASURING SPECIFIC HEAT.

289. I. Method by mixture. Four different methods of measuring the specific heat of substances have been proposed. They are known as (1) the method by mixture, (2) the method by fusing ice, (3) the method by condensing steam, and (4) the method by cooling. In the first of these, or the method of mixtures, the experiment is made in the following manner. Take a known mass of the substance of which the specific heat is desired, and heat it to a known temperature, then mix it rapidly with a known mass of water at an inferior temperature (say at 0°C), and notice the temperature of the mixture. If we are at liberty to suppose that none of the heat has been otherwise disposed of, we have at once all the means of determining the specific heat of the substance in question. Thus, let x denote the unknown specific heat of the substance, and let m be its mass, and t its temperature; also let M be the mass of water at 0°C with which it is mixed, and let θ be the temperature of the mixture. Then the quantity of heat lost by the substance will be $mx(t-\theta)$, while that gained by the water will be $M\theta$. Since the whole quantity of heat remains the same, the one of these expressions must equal the other. Hence $mx(t-\theta) = M\theta$, from which x may be easily found. As an example of this method, supposing that 3 kilogr. of mercury at 100°C have been mixed with 1 kilogr. of ice-cold water, and that the temperature of the mixture is 9°C , what is the specific heat of mercury? Here we have $m = 3$, $M = 1$, $\theta = 9$, $t - \theta = 100 - 9 = 91$: hence

$$3 \times 91 = 9; \quad \therefore x = \frac{9}{273} = .033 \text{ nearly:}$$

so that the specific heat of mercury is only $\frac{1}{80}$ th of that of water.

In this process it is assumed that the specific heat of mercury is constant between 100° and 9°C , or rather it is the mean specific heat within this range that is determined by the experiment.

A serious objection to this method consists in the unavoidable loss of heat which is likewise incapable of accurate measurement. For in the example given above the heat of the mercury is not all confined to the mixture, but part of it is spent:

1. In warming the vessel which contains the mixture,
2. In warming the agitator and thermometer,
3. In dissipation from the sides of the vessel;

and unless we have the means of estimating exactly the loss of heat from all these sources we shall not be able to obtain a good result.

290. II. Method by fusion of ice. The second method of measuring specific heat is by the fusion of ice. In this method we have an inner vessel *A* (Fig. 68) which contains the substance on which the experiment is made. This vessel is placed in the interior of a larger vessel *B*, the space between them being filled with melting ice. The vessel *B*, again, is in the interior of a still larger vessel *C*, the space between them being, again, filled as before with melting ice.



Fig. 68.

Since the exterior of the vessel *B* is at the temperature 0°C , we may imagine that the ice in this vessel will only melt through means of the hot substance which is placed in *A*. If

therefore we know not only the mass but the temperature of the substance in *A*, and also the quantity of ice which has been converted into water in consequence of this hot substance parting with its heat, we have the means of finding the specific heat of the substance in *A*. A stopcock connected with *B* serves to carry off the water formed through melting of the ice, and hence, by weighing this water, we know approximately the quantity of ice melted in *B*; and if we know the quantity of heat necessary to convert ice into water we can find the heat given out by the substance in *A*. The chief objection to this instrument is that we cannot measure accurately the amount of water produced, since a certain amount remains adhering to the ice.

Professor R. Bunsen (*Phil. Mag.* March, 1871) has devised a modification of the ice calorimeter for the purpose of measuring the specific heat of substances which can only be procured in small quantities.

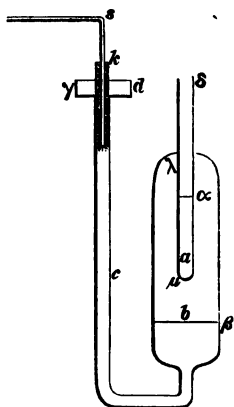


Fig. 69.

It consists of an inner glass vessel *a* fused into a larger cylindrical vessel *b* as in Fig. 69. From the vessel *b* proceeds the tube *c*, to the termination of which the iron collar *d* is fastened. The inner vessel *a* is filled from *a* to *μ*, as also the outer vessel *b* from *β* to *λ*, with water from which all the air has been removed by boiling; the remainder of the vessel *b* up to the level *γ* is filled with boiled mercury.

Before using the instrument it is necessary to obtain a cylinder of ice in the vessel *b* so as completely to surround the vessel *a*, and for this purpose the whole apparatus is placed in a large vessel and surrounded with

pure snow. When this operation is complete the scale-tube *s*, fitted accurately into the cork with fine sealing-wax, is then passed through the mercury in the collar *d* and made fast in the mouth of the tube *c* so that it (the scale-tube) becomes filled with mercury.

Our object being to ascertain the amount of heat which a small body gives up when cooled from its ordinary temperature to 0°C , let this body be dropped into the water contained in the vessel *a*, which is then closed with a cork at *δ* to prevent change of air. It is clear that all the heat which this body gives up is employed to melt ice. For the weight of the body is so small compared with that of the ice-cold water into which it is plunged, that the temperature of the latter never reaches 4°C ; the heated water will therefore be specifically heavier than that above it and will remain at the bottom. Thus none of its heat will be carried away by convection, and we may neglect that carried away by the conducting power of the water above it, this being very small. In fine, all the heat will go to melt ice in the vessel *b*; this melting will again cause a diminution of volume, and this in its turn will be indicated by the motion of the mercurial column in the scale-tube *s*.

As the experimental difficulties in using this calorimeter are considerable, the writer of this volume has suggested a modification of it which appears to answer well. In this the inner vessel *a* is still retained and used with water, but instead of being fused into an outer vessel that is filled with ice it is fused into a large thermometer bulb after the manner of Favre and Silbermann, so that while the inside of *a* contains water its outside is in contact with the mercury of the thermometer. The whole bulb is then enclosed in a copper envelope which surrounds without touching it, and this envelope is kept at the temperature

of 0°C by being surrounded by melting ice. The temperature of the large thermometer is recorded on a very open scale, so that a very small rise can easily be measured.

The experiment is conducted in the following manner:

The substance the specific heat of which we wish to determine is dropped as before into the water of the tube α , which is ice-cold to begin with. The heat is then rapidly communicated first to the water and from it to the mercury of the thermometer which surrounds the tube, and the rise of this thermometer is recorded on the stem.

A slight correction has to be made for the heat which is given out during the progress of the experiment by the (now) heated thermometer to the copper sphere which surrounds it, but this is easily obtained, and thus the instrument gives us a ready and accurate method of determining the relative specific heats of such substances as can only be procured in small quantity.

290 a. III. Method by condensation of steam. In 1886 Dr. J. Joly invented a 'steam calorimeter' by which extremely accurate results can be obtained. It consists of a thin metal chamber into which steam can be admitted at pleasure and in which is a cup-shaped platinum pan suspended from the arm of a balance by a wire that passes through a small hole in the cover of the chamber. On the pan is placed the substance under experiment, and after it has been weighed steam is quickly admitted, and the mass of steam which is condensed in heating the substance and the pan, and which is caught in the pan as water, is determined by another weighing. If then we know the amount of heat necessary to evaporate water at any temperature, and by a previous experiment have determined the amount of heat absorbed by the pan in any change of temperature, we can determine the specific heat of the substance.

291. IV. Method by cooling. The fourth means of estimating specific heat is by the method of cooling. If two substances be exposed to the same cooling influence it is manifest that the one which has the smaller specific heat will cool the faster. Thus, suppose that we have two thermometers with blackened bulbs of precisely the same size, the one being filled with mercury and the other with water; further, let these instruments both cool from a common temperature under precisely the same circumstances. It will be found that the mercurial thermometer will cool more than twice as fast as the water one. For although the mass of the mercury is more than thirteen times that of the water, yet the specific heat of mercury is only one thirtieth of that of water, and hence, while the same amount of heat leaves both instruments in one minute, yet this heat will produce on the water thermometer only thirteen thirtieths of that diminution of temperature which it produces on the mercurial one.

The idea of measuring the specific heat of bodies first originated with Black, who was also the discoverer of latent heat; and many important experiments have since been made on this subject by a number of observers.

SPECIFIC HEAT OF SOLIDS.

292. Some of the latest experiments in this branch of the subject have been made by Regnault, who used the method of cooling. In these experiments the substance was reduced to a fine powder and enclosed along with a delicate thermometer in a vessel which was exposed to the cooling influence. Although every precaution was used, the result of this process was not satisfactory; one objection was that the heat was not conducted sufficiently fast from

the powder to the sides of the vessel which contained it. Another is that the specific heat of the same substance in the solid state depends to some extent on the mechanical treatment which it has received. Regnault has also investigated the specific heat of various solid substances by the method of mixtures.

293. Rise of specific heat of solids with temperature. It was first shewn by the experiments of Dulong and Petit that *the specific heat of a solid is greater at a high temperature than at a low one.* The following table embodies the results of these experiments.

Substance.	Mean Specific Heat.	
	Between 0° and 100°C.	Between 0° and 300°C.
Iron	0.1098	0.1218
Zinc.	0.0927	0.1015
Antimony.	0.0507	0.0549
Silver	0.0557	0.0611
Copper	0.0949	0.1013
Platinum	0.0355	0.0355
Glass	0.1770	0.1990

It will be noticed that for all the substances in the above table the specific heat is greater at high temperatures, with the exception of platinum, for which the specific heat remains the same between the limits of the experiment. Probably the reason of this is that the highest temperature of experiment was very much below the melting-point of this metal, and it has been found by Regnault that the variation of specific heat with temperature is much more rapid when the substance approaches its melting-point. M. Pouillet, by means of the method of mixtures, has obtained the specific heat of platinum at still higher temperatures. His results are as follows—

Mean Specific Heat of Platinum.

Between 0° and 100°C	0.0335
" 0 " 300	0.0343
" 0 " 500	0.0352
" 0 " 700	0.0360
" 0 " 1000	0.0373
" 0 " 1200	0.0382

The constancy of the specific heat of platinum renders this metal serviceable as a pyrometer, and a piece of platinum may be used for estimating the temperature of a furnace. When it has attained the temperature of the furnace it is taken out and plunged into a known quantity of ice-cold water. By means of the rise of temperature produced it is easy to calculate approximately the temperature of the platinum, and hence of the furnace.

294. Circumstances which influence the specific heat of solids. The specific heat of a solid has been found to depend on the mode of aggregation of its molecules and on the nature of the mechanical action to which it has been subjected. *In general whatever augments the density diminishes the specific heat, and whatever diminishes the density augments the specific heat; and it is perhaps owing to expansion that the specific heat of a body increases with its temperature.* The more carbon is divided the greater is its specific heat. The following table exhibits the specific heat, in their different stages of aggregation, of carbonate of lime, sulphur, and carbon.

Carbonate of Lime.		Sulphur.	
Aragonite	0.2085	Recently melted	0.1844
Iceland spar	0.2085	Melted less than 2 months	0.1803
Chalk	0.2148	Melted less than 2 years .	0.1764
White marble	0.2158	Natural crystals	0.1776

Carbon.

Animal charcoal	0.2608
Wood charcoal	0.2415
Coke	0.2008
Graphite	0.2018
Diamond	0.1468

SPECIFIC HEAT OF LIQUIDS.

295. Regnault has determined the specific heat of a number of liquids by the following method. The liquid under experiment is contained in a reservoir *R* (Fig. 70) which is immersed in the middle of a bath, and by agitating the water of this bath a definite temperature is communicated to the liquid in *R*. By opening the stop-cock at *r*, and bringing to bear at the same time an

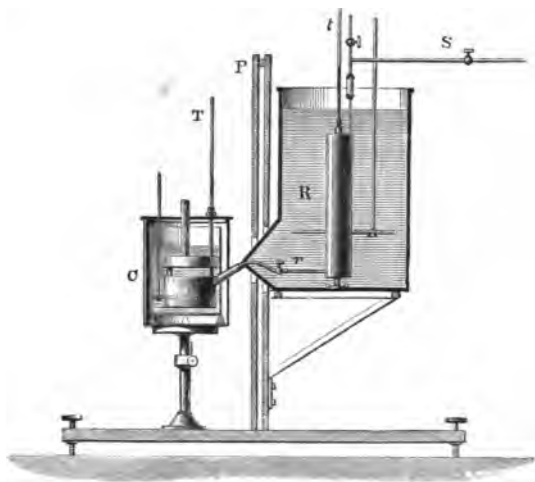


Fig. 70.

atmospheric pressure upon the liquid, it is driven through the tubes at *r* into a vessel contained in the calorimeter *C*. Having entered the calorimeter, and having disposed of its surplus heat, the temperature of the water of the calorimeter is observed by means of the thermometer *T*, and this affords the means of estimating the specific heat of the liquid. The calorimeter is defended by means of a screen *P* from the heat of *R*.

Generally speaking a substance when liquid has a greater specific heat than when solid, a fact which was discovered by Irvine. Thus the specific heat of ice is only one-half that of water.

296. Variation with temperature of the specific heat of liquids. *The specific heat of liquids increases in general with the temperature, and at a rate exceeding that of solids.* Thus bromine has between -6° and 10°C the mean specific heat 0.10513, while between 13° and 58° it has the mean specific heat 0.11294.

The specific heat of water at various temperatures has been studied by Regnault, who obtained the following result.

Mean Specific Heat of Water.

From 0° to 40°C		1.0013
" 0 " 80		1.0035
" 0 " 120		1.0067
" 0 " 160		1.0109
" 0 " 200		1.0160
" 0 " 230		1.0204

Professor Rowland has however shewn reason for thinking that the specific heat of water diminishes from 0°C to a minimum value between 30° and 35°C , and this diminution is confirmed by experiments (between 14° and 26°C) of Mr. Griffiths, who for this range expresses the specific heat by the formula

$$1 - 0.000266 (\theta - 15),$$

the unit of heat taken being that required to raise one gramme of water from $14\frac{1}{2}^{\circ}$ to $15\frac{1}{2}^{\circ}\text{C}$.

SPECIFIC HEAT OF GASES.

297. In this branch of our subject there are two sets of determinations to be made. We must find, in the first place, the specific heat of gas under constant pressure; and in the second place, the specific heat of gas under constant

volume. In Art. 332 it will be shewn how these two are connected together.

Many experimentalists have been engaged in these determinations. Before the time of Regnault one of the most exact researches was that of Delaroche and Bérard, which was crowned by the Academy of Sciences. These experimentalists produced a current of gas of uniform velocity which was first heated to 100°C by being passed through tubes enveloped in boiling water, and was then cooled in its passage through a calorimeter, to which it abandoned its excess of heat. It ought likewise to be mentioned that Joule made an accurate determination of the specific heat of air.

After many years' trials Regnault finally adopted a modification of the method of Delaroche and Bérard.

His apparatus was constructed so as to fulfil the following requirements—

1. To obtain a gaseous current of constant velocity, which velocity might also be regulated at will.
2. By means of a bath to give a determinate temperature to the gaseous current.
3. To have a calorimeter in which the gas would entirely dispose of its excess of heat.

In order to obtain a gaseous current of constant velocity the following arrangement was adopted. The gas, after being dried and purified, was forced into a large reservoir *R* (Fig. 71) of 35 litres capacity. A manometer attached to the reservoir at *m* indicated the pressure of the gas. The reservoir was surrounded by a large mass of water agitated by means of an annular plate *a*. The gas would thus take the temperature of this water—this temperature being denoted by the thermometer *T*. Suppose, in the first place, that the reservoir is filled with gas, and that the stop-cock *l* is shut. Opening now the stop-cock at *l* this

gas will escape through the tube shewn in the figure, passing spirally through an arrangement at *S*, by which a certain high temperature is given to it, then parting with this excess of heat to a calorimeter at *C*, and ultimately escaping (say) into the air. At the end of the experiment suppose that the stop-cock at *l* is once more shut. Knowing the pressure and temperature of the gas in *R* at the beginning and end of the experiment, if the chemical constitution of the gas be known, and if it obeys Boyle's law, the mass of gas passed through the calorimeter will be known. If Boyle's law do not hold, it is yet possible, though with more difficulty, to ascertain the

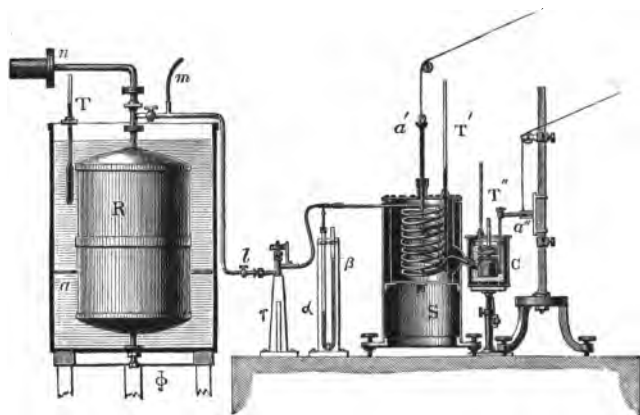


Fig. 71.

mass of gas used, but into the details of the method of doing so we will not enter. The mass of gas consumed during the experiment is thus known, but in order to obtain a definite result something more is necessary; the velocity of the current of gas through the apparatus ought to be constant throughout the experiment. It is clear that without some special arrangement this current will

not be constant, because the excess of pressure in the reservoir R will be greater at the commencement of the experiment than at the end of it, when a quantity of this gas has been used. There is, however, an arrangement r by means of which the opening through which the gas escapes from the reservoir into the apparatus may be enlarged or contracted at pleasure. A manometer to the right of r , having one of its limbs open to the atmosphere, indicates the excess of pressure of the gas in the tube, and if the screw at r is turned in such a manner that throughout the whole experiment the excess of pressure denoted by this manometer is constant, then will the velocity of the current be constant also. Agitators a' , a'' are attached to the source of heat and the calorimeter, and it was ascertained by Regnault that the gas in passing through S really attained the temperature (indicated by T') of the fluid (oil) in S . It was further ascertained that the gas lost none, or extremely little, of its heat in passing between S and the calorimeter, and that in passing through the vessel of the calorimeter, which was arranged in a spiral form so as to present as much surface as possible to the surrounding water, the gas issued with a temperature the same as that of the water of the calorimeter indicated by the thermometer T'' . Finally it was ascertained that the pressure of the gas was as nearly as possible the same before its entrance into the calorimeter and after its exit therefrom.

To simplify matters we may suppose the pressure of the outward air constant throughout the experiment.

In this experiment therefore a known mass of gas having a known temperature (that of the bath) was made to pass with a constant velocity and at a constant pressure through the calorimeter, where it was reduced in temperature to that of the water of the calorimeter. The specific heat of a gas under constant pressure was thus found.

298. Results of Regnault's experiments. The following facts were determined by these experiments:—

1. *The specific heat of a given mass of a gas which is approximately perfect, and which therefore follows the gaseous laws previously indicated (Art. 148), does not vary with the temperature of the gas.*

2. *The specific heat of a GIVEN MASS of such a gas does not vary with the pressure or density of the gas, and hence the specific heat of a GIVEN VOLUME of such a gas varies as its density.*

3. *The specific heats of equal volumes of the simple and incondensable gases are equal, but this equality does not hold for gases easily condensed, such as chlorine and bromine. It holds, however, for compound gases which are formed without condensation, such as hydrochloric acid and nitric oxide.*

4. *These laws do not hold for condensable gases—the specific heat of carbonic acid gas, for instance, increases with the temperature.*

299. The following table is derived from Regnault's determinations.

Specific Heat of Gases and Vapours under Constant Pressure.

Gas or Vapour.	Equal	
	Vols.	Masses.
Air	0.2375	
Oxygen	0.2405	0.2175
Nitrogen	0.2368	0.2438
Hydrogen	0.2359	3.4090
Chlorine	0.2964	0.1210
Bromine	0.3040	0.0555
Nitrous oxide	0.3447	0.2262
Nitric oxide	0.2406	0.2317
Carbonic oxide	0.2370	0.2450
Carbonic acid	0.3307	0.2169
Bisulphide of carbon	0.4122	0.1569

Gas or Vapour.	Equal	
	Vols.	Masses.
Ammonia	0.2996	0.5084
Marsh gas	0.3277	0.5929
Olefiant gas	0.4160	0.4040
Chloride of arsenic	0.7034	0.1122
Chloride of silicon	0.7778	0.1322
Perochloride of titanium . .	0.8564	0.1290
Perochloride of tin	0.8416	0.0939
Sulphurous anhydride	0.3414	0.1554
Hydrochloric acid	0.2333	0.1852
Sulphuretted hydrogen . . .	0.2857	0.2432
Water	0.2989	0.4805
Alcohol	0.7171	0.4534
Wood spirit	0.5063	0.4580
Ether	1.2266	0.4797
Chloride of ethyl	0.6096	0.2738
Bromide of ethyl	0.7026	0.1896
Sulphide of ethyl	1.2466	0.4008
Cyanide of ethyl	0.8290	0.4261
Chloroform	0.6461	0.1567
Dutch liquid	0.7836	0.2293
Acetic ether	1.2184	0.4008
Benzole	1.0114	0.3754
Acetone	0.8264	0.4125
Oil of turpentine	2.3776	0.5061
Terchloride of phosphorus . .	0.6395	0.1347

In the first column of this table the common volume is that occupied by one kilogramme of air, while in the second column the common mass is one kilogramme. Also the specific heat of one kilogramme of liquid water is taken as the unit, so that the heat required to raise a kilogramme of atmospheric air one degree under constant pressure is only 0.2375 of that required to raise a kilogramme of water one degree.

200a. Specific Heat at constant volume. No attempts were made to determine by direct experiment the specific heat of a gas of constant volume until 1889, when Dr. Joly employed a differential form of his steam-calorimeter (Art.

290a) in which hollow spheres of equal mass and external volume hang in the calorimeter from both pans of the balance, one sphere being empty and the other containing the gas under experiment at any desired pressure. The specific heat at constant volume seems to increase with the pressure for air and carbonic acid, and is about 0.1721 for both under 19.5 atmospheres pressure: for hydrogen the reverse seems the case, and its specific heat at mean pressures is about 2.402.

300. Influence of the state of a substance on its specific heat. *The same body has a higher specific heat in the liquid than in the solid state, while in the gaseous condition, again, its specific heat is less than when it is liquid.* Thus, for instance, the specific heat of water is twice as great as that of ice, and more than twice as great as that of steam.

The following table exhibits the dependence of the specific heat on the physical state of the substance.

Substance.	Specific heat.		
	Solid.	Liquid.	Gaseous.
Water	0.5040	1.0000	0.4805
Bromine	0.0833	0.1060	0.0555
Tin	0.0562	0.0637	
Iodine	0.0541	0.1082	
Lead	0.0314	0.0402	
Alcohol		0.5475	0.4534
Bisulphide of carbon		0.2352	0.1569
Ether		0.5290	0.4797

ATOMIC HEAT.

301. Atomic heat of simple bodies. In 1819, Dulong and Petit made experiments on the specific heat of thirty elementary bodies, and discovered that for equal masses of each substance the specific heat is in the inverse proportion of the atomic weight. Regnault has made a number of ex-

periments with the view of testing the accuracy of this law, and the following results have been chiefly obtained by him. (The atomic weights are those given in Williamson's Chemistry for Students, p. 100.)

Elements.	Specific heat of equal masses.	Atomic weight.	Product of specific heat into atomic weight or atomic heat.
Sulphur . . .	0.1776	32	5.6832
Tellurium . .	0.0474	129	6.1146
Magnesium . .	0.2499	24	5.9976
Zinc . . .	0.0955	65	6.2075
Cadmium . . .	0.0567	112	6.3504
Aluminium . .	0.2143	27.5	5.8932
Iron . . .	0.1138	56	6.3728
Nickel . . .	0.1091	58.5	6.3823
Cobalt . . .	0.1070	58.5	6.2595
Manganese . .	0.1140	55	6.2700
Tin . . .	0.0562	118	6.6316
Tungsten . . .	0.0334	184	6.1456
Copper . . .	0.0951	63.5	6.0389
Lead . . .	0.0314	207	6.4998
Mercury (solid)	0.0319	200	6.3800
Platinum . . .	0.0324	197	6.3828
Palladium . . .	0.0593	106.5	6.3154
Rhodium . . .	0.0580	104	6.0320
Osmium . . .	0.0306	199	6.0894
Iridium . . .	0.0325	197	6.4025
Iodine . . .	0.0541	127	6.8707
Bromine (solid)	0.0843	80	6.7440
Potassium . .	0.1696	39	6.6144
Sodium . . .	0.2934	23	6.7482
Lithium . . .	0.9408	7	6.5856
Arsenic . . .	0.0814	75	6.1050
Antimony . . .	0.0508	122	6.1976
Bismuth . . .	0.0308	210	6.4680
Thallium . . .	0.0336	203	6.8208
Silver . . .	0.0570	108	6.1560
Gold . . .	0.0324	196	6.3504

It appears from this table that *the product of the specific heat by the atomic weight is very nearly the same for all the elementary bodies.* The differences in this product may be accounted for by supposing that the different elements ex-

perimented on were not all in the same physical state, some of these being near their melting-points and others at a great distance from them.

It will be observed that neither carbon, boron, nor silicon appear in the above table, although these three substances are well known to be elementary bodies. Until recently it was imagined that those three solid elements had a very different atomic heat from all the others, crystallised silicon giving 4·8, crystallised boron 2·7, and crystallised carbon 1·8. But in the winter of 1871–1872 Dr. H. F. Weber, on analysing these various determinations, arrived at the following conclusion:—*The different observers have determined the specific heats of these elements for entirely different intervals of temperature; and the greater the interval of temperature for which the specific heat is determined, the greater is the number representing that specific heat.*

He was thus led to undertake an extensive series of experiments, from which he has obtained the following important results.

1. The values of the specific heats of the elements carbon, boron, and silicon change with the temperature; these values gradually increase with an increase of temperature until a point is reached at which they are constant. This point is situated at about 600°C for carbon and boron, at about 200°C for silicon. The specific heat of carbon at 600°C is about seven times, that of boron about two and a half times, as great as at –50°C.

2. The constant final values for the specific heats of carbon, boron, and silicon are in round numbers 0·46, 0·50, and 0·205 respectively. The products of these numbers, multiplied into the atomic weights 12, 11, and 28, are 5·5, 5·5, and 5·8—values which are in keeping with the atomic heats of the metals and of the other non-metals.

3. All opaque modifications of carbon (graphite, dense

and porous) have the same specific heats. From a thermal point of view there are, below a red heat, but two allotropic modifications of carbon, the opaque and the transparent. The specific heats of these two modifications differ considerably at low temperature; with increasing temperature, however, their values are gradually equalised, until at about 600° they become the same.

302. Atomic heat of compound bodies. Neumann and Regnault have determined that *in all compound bodies of similar atomic composition the specific heats are inversely as the atomic weights*. The product of the specific heat into the atomic weight for one class of compounds may however be different from that for another class of compounds. Thus Regnault gives the following table for the specific heat of bichlorides.

	Specific heat.	Atomic weight.	Product of specific heat into atomic weight.
Chloride of Barium (BaCl^2) .	0.0896	208	18.64
„ Strontium (SrCl^2) .	0.1199	158.5	19.00
„ Calcium (CaCl^2) .	0.1642	111	18.23
„ Magnesium (MgCl^2) .	0.1946	95	18.49
„ Lead (PbCl^2) . .	0.0664	278	18.46
Perchloride of Mercury (HgCl^4)	0.0689	271	18.67
Chloride of Zinc (ZnCl^2) . .	0.1362	136	18.52
Perchloride of Tin (SnCl^4) . .	0.1016	189	19.20

For carbonates we have the following table.

	Specific heat.	Atomic weight.	Product of specific heat into atomic weight.
Carbonate of Lime (CaCO^3) .	0.2086	100	20.86
„ Barytes (BaCO^3) .	0.1104	197	21.75
„ Strontium (SrCO^3) .	0.1448	147.5	21.36
„ Iron (FeCO^3) . .	0.1934	116	22.43

It thus appears that the numbers of each table agree very well together, but the numbers of the one table do not agree well with those of the other.

Finally Kopp has made a great many observations on the atomic heat of compound bodies, and has come to the conclusion that the atomic heat of a compound substance is nearly equal to the sum of the atomic heats of its components, but that it is necessary to assume that oxygen and hydrogen have smaller atomic heats than the other elementary bodies.

CHAPTER X.

Latent Heat.

303. It has been already remarked (Art. 91) that a large quantity of heat is required by bodies in order to enable them to pass from the solid into the liquid, or from the liquid into the gaseous state. This heat, which is absorbed by bodies during their passage from one state to another, does not as a rule manifest itself by producing an increase of temperature, and it has on this account been called latent heat; so that we may with much propriety affirm regarding water—

Water at 0°C = ice at 0°C + latent heat of liquefaction ;
or regarding steam—

Steam at 100°C = water at 100°C + latent heat of vaporisation.

Latent heat was discovered by Black, and the principles of this branch of science were first taught by him in 1762.

LATENT HEAT OF LIQUEFACTION.

304. Latent heat of water. Black first attempted to

measure the latent heat of water in the following manner. He suspended in a room of the temperature of 64° Fahr. two similar glass vessels, one containing melting ice and the other ice-cold water; and he noticed that at the end of half an hour the water had attained the temperature of 40° Fahr., while the ice did not reach this temperature until ten hours and a half had elapsed. He argued that the quantity of heat absorbed by the vessels was very nearly proportional to the time of exposure, and by this means he attempted to estimate the amount of heat absorbed by ice while passing into the state of water. Afterwards Black adopted the method of mixtures. The following example will illustrate this method of experiment.

It is found that a kilogramme of water at 100°C mixed with a kilogramme of water at 0°C , gives two kilogrammes of water at a temperature equal, as nearly as possible, to 50°C , this temperature being the mean of those of the two components; if however a kilogramme of ice at 0°C be mixed with a kilogramme of water at 100° , we have two kilogrammes of water at $10^{\circ}\cdot6\text{C}$ only. A correct experiment of this kind gives us the means of measuring the latent heat of water. For we see that when equal masses (one kilogramme each) of boiling and ice-cold water are mixed together, we have water at 50° , while when the same masses of boiling water and melting ice are mixed together we have water at $10^{\circ}\cdot6$ only. There is thus a difference in the total heat of the two mixtures equal to that required to raise two kilogrammes of water from $10^{\circ}\cdot6$ to 50° , or through a range of $39^{\circ}\cdot4\text{C}$. Now since the heat of the boiling water was the same in each experiment, this difference must necessarily represent the heat required to liquefy one kilogramme of ice. We thus see that it requires as much heat to liquefy one kilogramme of ice at 0° as it does to raise two kilogrammes of water through a range of $39^{\circ}\cdot4\text{C}$, or one kilogramme of

water through a range of $78^{\circ}\cdot8$ C, or 78·8 kilogrammes of water through a range of 1° C.

If we take as our unit of heat the quantity of heat necessary to raise one kilogramme of water through 1° C, we have therefore the latent heat of water represented by 78·8.

305. Many distinguished philosophers have attempted since the days of Black to estimate the latent heat of water, and amongst these we may name Provostaye and Desains, Regnault, and finally Person. The experimental arrangements necessary for the estimation of latent heat are however so similar in principle to those required for estimating specific heat, that it will be unnecessary to give the details of the various experiments—let us rather state the results obtained. Provostaye and Desains used melting ice in their experiments, while Regnault employed both snow and melting ice. The united result of these experiments was to give 79·25 units of heat as the most probable value of the amount required to liquefy one kilogramme of ice.

306. The experiments of M. Person are well worthy of an attentive study, as affording at the same time evidence that the change which takes place when ice becomes water is to some extent gradual and not quite abrupt.

M. Person in his experiments employed ice at a temperature inferior to its melting-point.

In one of these the ice was at -2° C, and it may be desirable to describe here in a few words how the latent heat of liquefaction of ice is to be derived from an experiment where the ice used is below its melting-point. When such ice is melted we may imagine, for convenience sake, that the heat applied has two separate offices to perform. First of all, it has to raise the ice from its present temperature to the melting-point; and secondly, it has to liquefy this melting ice. It is the quantity of heat requisite to perform this latter office that is generally regarded as a measure of the latent

heat, while that necessary to perform the former office may be estimated by knowing the temperature of the ice used and the specific heat of this substance. Thus we have seen (Art. 295) that the specific heat of ice is one-half that of water, or 0.5. In the above experiment, therefore, where the ice was at -2°C , we might imagine one unit of heat necessary to raise the ice from this temperature to 0°C ; while the remainder of the whole heat required to melt the ice might be taken to denote the latent heat of liquefaction. Now on this supposition Person found that the latent heat of liquefaction, as determined by this and similar experiments, was 80 units instead of 79.25, as found by Regnault and others.

M. Person, in continuing his investigations, was able satisfactorily to account for this difference. He found that a kilogramme of ice at -2°C requires two units of heat instead of one to raise it to 0°C ; in fact it would appear as if the ice between -2°C and 0°C had already begun to absorb part of the heat of liquefaction, and thus that the absorption of latent heat in order to be complete required a certain range of temperature.

Presuming this to be the case with ice, it will at once be seen that, as far as such observations are concerned, latent heat simply resolves itself into an enormous increase of specific heat between certain narrow limits of temperature, and that in truth latent heat begins to be absorbed when the specific heat begins to increase; or, in other words, these two terms are only two different ways of expressing one and the same action.

We thus derive from these experiments of Person a basis for the theory of the gradual liquefaction of ice—a theory which we have already seen (Art. 101) has been applied with much success by Principal Forbes in order to account for the phenomenon of regelation.

307. Latent heat of other liquids. M. Person has made numerous experiments on the latent heat of other liquids besides water, and has obtained the following results :—

Substance.	Latent heat of one kilogramme.	
	In thermal units.	Water = 1.
Water	79·25	1·000
Phosphorus . .	5·034	0·063
Sulphur	9·368	0·118
Nitrate of Soda .	62·975	0·794
Nitrate of Potassa	47·371	0·598
Tin	14·252	0·179
Bismuth	12·640	0·159
Lead	5·369	0·067
Zinc	28·13	0·355
Cadmium	13·66	0·172
Silver	21·07	0·266
Mercury	2·83	0·035

LATENT HEAT OF VAPORISATION.

308. Latent heat of steam. Black, the discoverer of latent heat, was the first who attempted to estimate the latent heat of steam. The subject has since engaged the attention of many eminent men, and amongst others of Watt, Rumford, Despretz, Southern, and Clément and Désormes. Finally, Regnault has discussed the subject with great exactness.

The object of Regnault's experiments was to determine the quantity of heat which must be furnished to one kilogramme of water at 0°C in order to convert it wholly into saturated vapour at a given pressure; that is to say, how much heat must be supplied to this kilogramme of water in order, first, to raise its temperature from 0°C to a certain temperature without evaporation; and, secondly, to evaporate it entirely at that temperature and under the pressure which corresponds to it.

The following was the experimental method pursued:

by Regnault. In order to obtain the formation of aqueous vapour at a constant high temperature, the same arrangement was adopted as that used in making experiments on the pressure of aqueous vapour; that is to say, the water was made to boil under the pressure of an artificial atmosphere, while the vapour so formed was condensed in a condenser almost as fast as it was furnished. The formation of aqueous vapour at a high and constant temperature might thus be obtained (see Fig. 33).

To this arrangement in the present experiment a system of two calorimeters was added. In this experiment we may therefore suppose the calorimeters to be supplied at one end with saturated steam of a given constant pressure and temperature, which, having passed through the calorimeter, is condensed into water of a known temperature, having in the meantime given out a measurable quantity of heat. Suppose, for example, that a kilogramme of steam at 100°C in passing through a calorimeter filled with water at -1°C heated up 637 kilogr. of water from this temperature to 0°C , the condensed water of the steam having also the temperature 0°C , then from this experiment Regnault conceived himself entitled to suppose that the total heat (as he terms it) of steam at 100°C is 637. He conceived that he was entitled to infer that if a kilogramme of water at 0°C was first of all heated without evaporation to 100°C , and at that temperature totally converted into steam, the total quantity of heat necessary to do all this would be 637 units. We shall see in a subsequent part of this work (Art. 386) that this inference is quite correct; in the meantime we content ourselves with defining what Regnault meant by the total heat of steam, and in stating by what experimental means he imagined he had obtained it.

Regnault also made experiments at low pressures by another method.

The following table embodies the results of all his experiments:—

Total Heat of Steam.

Temperature of the saturated vapour.	Total Heat.
0°	606.5
10	609.5
20	612.6
30	615.7
40	618.7
50	621.7
60	624.8
70	627.8
80	630.9
90	633.9
100	637.0
110	640.0
120	643.1
130	646.1
140	649.2
150	652.2
160	655.3
170	658.3
180	661.4
190	664.4
200	667.5
210	670.5
220	673.6
230	676.6

The latent heat of steam at any temperature is very easily derived from the total heat given in this table. Thus it takes 637 units first to heat a kilogramme of water at 0° to 100° and then to evaporate it at that temperature, but it takes as nearly as possible 100 units to heat it from 0° to 100°; so that $637 - 100 = 537$ units denote the latent heat of steam at 100°C.

309. Latent heat of other vapours. Andrews and Favre & Silbermann have made numerous experiments on this subject. The following table embodies the results derived by Andrews—the liquid is supposed always to be evaporated at the temperature of its boiling-point:—

Latent Heat of Vapours.

Substance.	Latent heat of one kilogramme.	
	In thermal units.	Steam = 1.
Water	535·9	1·000
Wood spirit	263·7	0·492
Alcohol	202·4	0·378
Formiate of methyl	117·1	0·219
Acetate of methyl	110·2	0·206
Formic ether	105·3	0·196
Acetic ether	92·68	0·173
Ether	90·45	0·169
Bisulphide of carbon . . .	86·67	0·162
Oxalic ether	72·72	0·136
Terchloride of phosphorus .	51·42	0·096
Iodide of ethyl	46·87	0·087
Iodide of methyl	46·07	0·086
Bromine	45·60	0·085
Perchloride of tin	30·53	0·057

If we compare this table with that of the latent heat of liquids, we shall find that in both water stands at the head of the list; that is to say, the latent heat of liquefaction of ice is greater than that of any other solid, also the latent heat of vaporisation of water is greater than that of any other liquid.

BOOK III

ON THE NATURE OF HEAT, ITS SOURCES, AND ITS CONNEXION WITH OTHER PROPERTIES OF MATTER.



CHAPTER I.

Remarks on Energy—Historical and Preliminary.

310. IDEAS regarding the nature of Heat have recently undergone a great change. Formerly this agent was regarded as a species of matter, but of the class of the imponderables, since no evidence of the weight of Heat could be obtained, inasmuch as a hot body does not weigh more than the same body when cold ; but very lately scientific opinion has unanimously decided that Heat is not a kind of matter, but a kind of energy. Contemporaneously with this change in our conception of Heat, a great general law, which binds together the various kinds of energy, invisible and visible, has become known under the title of the Conservation of Energy. As this law is intimately connected with that conception which regards Heat as a kind of energy, we shall begin this branch of our subject by a short account of this great and important principle.

311. *Perpetual motion.* Almost from time immemorial certain curious and perplexing questions in various branches

of knowledge have thrust themselves prominently forward, so as almost to haunt the human mind.

In chemistry the famous speculation was the possibility of transmuting other metals into gold ; while in physics it was the possibility of perpetual motion.

These questions may appear visionary, but they have not been without an indirect influence upon the progress of knowledge, and without doubt an intelligent denial of the possibility of perpetual motion leads at once to an exact knowledge of the fundamental principles of the science of energy.

We shall hereafter see that there are two forms of the idea of perpetual motion : one of these may be very easily stated. The use of any machine, it is well known, is to do work. We need not here define 'work,' for its meaning will at once be understood. Now to do some kind of work is the object of every machine. But in order to keep a machine going it has always been found necessary to perform, either continuously or periodically, some operation upon this machine. Thus you must yourself keep constantly working at a turning-lathe, or a coffee-mill, in order that either of these machines may do work ; and though a clock may go for a long time by itself, yet it has to be wound up periodically. When we come to a steam-engine, or even to a living being, such as a man or a horse, the case is somewhat different ; yet the difference is not very great. Both of these have to be fed regularly, the one with fuel and the other with food, in order that they may continue to work.

Now in one form of the idea of perpetual motion it is thought possible to construct a machine which can go on doing external work without the application of any external agency, either constant or intermittent. May there not, it is said, be some hidden, unknown material agent, that gives us this great desideratum ? It is the most difficult thing

in the world to prove a negative, especially in such a case as this, for our knowledge of the various forces of matter is extremely limited. It is only in the case of a clock or similar machine that we can prove the impossibility of perpetual motion of this kind ; in other cases we are driven simply to deny this possibility. But this denial, intelligently made, leads us at once to the principle of the Conservation of Energy, which asserts that the amount of energy in a material system left to itself is a constant quantity, and that the only change is from one form of energy to another ; so that, do what you may, you can only get a definite and limited amount of work out of any machine that is not supplied with energy in some other form.

312. Definition of energy. I. Kinetic energy. Before proceeding any further let us attach a more definite idea to the word 'work' ; and to enable us to do so we may call to our aid the all-pervading force of gravity, against the action of which our efforts are so frequently directed. Let us agree to consider a kilogramme raised up vertically one mètre in vacuo against gravity as representing the performance of one unit of work. It is necessary to say in vacuo ; because, for example, if the weight be made of wood and the medium be water, it is evident that we perform no work by lifting the wood one foot higher in the water ; on the other hand, we should perform work by causing it to sink. A kilogramme raised one foot in vacuo against gravity is taken as unit of work performed.

Now according to this standard it is easy to perceive that the kilogramme raised two mètres in height will represent the performance of two units of work, if raised three mètres the performance of three units, and so on. Further, a mass of two kilogrammes raised one mètre will denote two units of work done, and a mass of three kilogrammes raised one mètre three units, and so on. In fine, if the mass of matter

be m kilogrammes, and if it be raised h mètres against gravity, which we may suppose to be the same for all points at the earth's surface, then the work done $= m h$ units.

313. Let us now study the action of gravity in producing velocity; and in order to do so let us suppose that the mètre and the second are our units of space and time, while our unit of velocity is represented by a body moving at the rate of one mètre in a second, and our unit of acceleration is the production of unit velocity by a force acting for one second. Under this convention the intensity of gravity, or g , will be denoted by 9.8, since when a body is allowed to fall under the action of gravity for one second, it is found to have acquired the velocity of 9.8 mètres per second. If we consider how far this body has fallen in one second in order to acquire this velocity, we shall find the distance to be 4.9 mètres; and if, on the other hand, we project a body upwards with the velocity of 9.8 mètres per second, it will rise against gravity 4.9 mètres in height. A kilogramme projected vertically upwards with the velocity of 9.8 mètres per second is therefore capable of doing 4.9 units of work before it comes to rest.

Again, it is found that a body, allowed to fall for two seconds under the influence of gravity, will have acquired the velocity of 19.6 mètres per second, and that during this time it will have fallen 19.6 mètres. A kilogramme projected vertically upwards with the initial velocity of 19.6 mètres per second, will therefore rise 19.6 mètres in height, and will do 19.6 units of work before it comes to rest.

We thus see that a double velocity enables the body to do four times as much work—in fine, in order to find out how much work a body one kilogramme in mass projected upwards with the velocity v is capable of doing, we have only to ask how high it will rise. This will be given by the following formula:—

$$\text{Height of Ascent or Work Done} = \frac{v^2}{19.6}. \quad (A)$$

Thus, if the velocity be 9.8, we have by this formula—

$$\text{Work} = \frac{(9.8)^2}{19.6} = 4.9;$$

but if the velocity be 19.6, we have—

$$\text{Work} = \frac{(19.6)^2}{19.6} = 19.6 \text{ as already stated.}$$

314. A little consideration will shew us that it is not necessary for the body to be moving with this velocity *vertically upwards* in order to be capable of doing this work; indeed, we have only selected the force of gravity as one of the most prominent forces *against* which work is done; but the moving body may likewise be made to do work *against* a spring, or even by means of a single fixed pulley or otherwise it may be made to raise another body *against* gravity. In fact, taking the words 'work done' in their most general sense, as representing space moved over against the action of any force, we see that the above formula (A) will hold good without reference to the direction in which the body is moving; and if we consider the kilogramme as denoting the unit of mass, we have the following general expression for the work capable of being done against any force by a body of mass m and velocity v —

$$\text{Work} = \frac{mv^2}{19.6}; \quad (B)$$

the unit of work being always the amount represented by raising one kilogramme one mètre against terrestrial gravity, or the *kilogrammètre* as this is termed. It ought to be borne in mind that if the force against which the work is done is much more powerful than gravity, then a comparatively small space passed over against the action of this force will denote a large amount of work. Thus,

for instance, if the force were constant and ten times as powerful as gravity, then a décimètre passed over against this force would be equivalent to a mètre against gravity. A body, such as a kilogramme, moving with a certain velocity may therefore be said to have a certain amount of energy¹ stored up in it in virtue of this velocity. This energy is termed *energy of motion*, or *kinetic energy* (*κίνησις*, *motion*).

315. II. Potential energy. Suppose now that this kilogramme moves vertically upwards with the initial velocity of 9·8 mètres per second, it will rise, we have seen, to the height of 4·9 mètres. When this height has been attained the velocity is all spent, and the body may be supposed to be for an instant at rest. Its *kinetic energy* is therefore all spent, since it has no velocity; but this has not been spent without some equivalent advantage being attained: the *kinetic energy* has in fact been spent in acquiring for the body a *position of advantage with regard to the force of gravity*, in virtue of which, when it falls to the point of projection, it will have reacquired the same amount of velocity, and therefore of kinetic energy, with which it originally started upwards. When the kilogramme has attained its extreme height of 4·9 mètres it has therefore *converted its energy of motion, or kinetic energy, into energy of position, or potential energy* (an expression first generalised by Rankine), and when it has again fallen it has *reconverted its potential energy into kinetic energy*.

There is thus as much energy in the kilogramme at the summit of its flight as at the moment of its discharge, only it is of a different kind in the two cases, being in the first potential and in the second kinetic energy; and, further, at any intermediate point of its course its energy is partly

¹ The term 'Energy' is due to Young: it means the power of doing work against gravity or any other force.

potential and partly kinetic ; but the sum of these two kinds of energy is constant throughout its range, so that in the varying motion of the kilogramme there is neither creation nor destruction of energy, but simply a transmutation from one form to another.

316. The case of a pendulum is almost precisely similar to that just mentioned, for when the bob of a pendulum is passing its lowest point its energy is all kinetic ; while at its highest point the energy is all potential. We may pass on at once from the case we have considered to any machine, and assert that the energy of such a machine left to itself, and neither doing work upon other bodies nor having work done upon it, is strictly constant and limited, although it may vary from kinetic to potential, and from potential back again to kinetic, according to the geometric laws of the machine. As far as regards the combinations of ordinary mechanics this principle was clearly enunciated by Newton, and was even to some extent recognised by Galileo.

By both these philosophers a machine was regarded not as a means of creating energy, but rather of transforming it from a less convenient to a more convenient kind ; and if we study the mechanical powers, as they are called, we shall find their office to be strictly this. The truth of this will be seen at once from a very simple illustration. If we take a lever, one of whose arms is twice as long as the other, a two-kilogramme mass at the end of the short arm will balance a one-kilogramme mass at the end of the long one ; but the one-kilogramme must fall two mètres in order that the two-kilogrammes may rise one mètre. Now according to the definition of 'work' already given, the work spent upon the long arm by the one-kilogramme mass falling will be two units, while that gained by the short arm rising will also be two units.

The product of the weight into the space moved over against gravity is the same for both arms ; but while the space-factor of this product is the larger one for the long arm, the weight-factor is the larger one for the short arm.

317. Functions of a machine. It thus appears that all we can do by the lever or the other mechanical powers is to increase the one factor at the expense of the other—that is to say, either to gain force by losing space, or to gain space by losing force. We may generalize this statement so as to make it applicable to all possible machines, and we may view these as instruments which when supplied with energy in one form convert it into other forms according to the law of the machine.

318. Conversion of mechanical energy into heat. It is not in ordinary mechanics that the difficulty of recognising the principle of the conservation of energy is found, but rather when visible motion has been transformed into molecular motion, or when the opposite transformation has taken place. Thus, for instance, when an anvil is struck by a hammer, what becomes of the energy of the blow? or when a railway train is stopped by the brake, what becomes of the energy of the train?

319. The true explanation of this difficulty has done more than anything else to forward the theory of the conservation of energy, and it is only of late years that the problem has been completely solved.

In considering the subject of percussion and friction, two simultaneous phenomena claim our attention. In the first place, the energy of the hammer and of the railway train disappear from the immediate cognisance of our senses—from that category which embraces visible potential and visible kinetic energy.

In the next place, by repeated strokes of the hammer upon the anvil we have the production of heat, nay even

of a red heat if the process be conducted sufficiently long and be sufficiently rapid ; and in like manner the stoppage of a railway train produces heat ; indeed we may see sparks flying out from the brake-wheel on a dark night.

For a long time this production of heat was regarded as inexplicable, because, heat being looked upon as a species of matter, it could not be imagined where all this heat came from. The only sort of explanation was, that in the processes of friction and percussion heat might be drawn from neighbouring bodies, or there might be a diminution in the thermal capacity of the two bodies acting on each other so that caloric was supposed to be squeezed, or rubbed, out of them, although it is not easy to see why the same effect should take place with two such different actions as friction and percussion. Davy, about the end of last century, was one of the first to refute this explanation by a very simple experiment. This consisted in rubbing two pieces of ice violently together until it was found that both were nearly melted by friction. The explanation of a diminution in thermal capacity was evidently inapplicable in this experiment, since water contains more heat than ice ; and other experiments performed by Davy combined to shew that the heat produced in such cases is not abstracted from neighbouring bodies. The result derived by Davy from these experiments was that heat implies a kind of motion of the corpuscles of bodies.

About the same time Count Rumford was engaged in boring cannon at the arsenal in Munich, and was struck with the very great amount of heat developed by this operation ; the source of this heat appeared to him to be inexhaustible, and he was therefore led to attribute it to motion.

Rumford, moreover, estimated approximately the quantity of heat produced by a definite amount of mechanical

energy, and pointed out that the agitation of liquids, such as churning, might form a very good means of determining the mechanical equivalent of heat. A complete determination of this equivalent was however reserved for Joule, but his experiments will form the subject of another chapter.

320. Conversion of heat into mechanical energy.

The converse problem, or the rationale of the conversion of heat into mechanical energy, was first undertaken by Carnot, a French philosopher. He shewed that mechanical effect is only produced by heat when there is a transference of heat from a body of higher to one of lower temperature. He likened, very ingeniously, the mechanical power of heat to that of water, shewing that just as a body of water at the same level can produce no mechanical effect, so neither can bodies at the same temperature produce any mechanical effect; and just as you must have a fall of water from a higher to a lower level in order to obtain mechanical effect, so likewise you must have a fall of heat from a body of higher to one of lower temperature. Carnot, in his researches, adopted the old or material theory of heat, and his principle therefore required to be modified so as to suit the dynamical theory. This was done nearly simultaneously by Rankine, Clausius, and Lord Kelvin. Further remarks on this subject we must defer to a future chapter.

321. Various principles of the science of energy.

It may be desirable at this stage to distinguish between three principles or laws connected with energy. The first of these is the principle of the conservation of energy, which asserts that energy is as indestructible as matter itself, and as a whole is neither created nor destroyed, but merely changes its form.

The second problem embraces the laws which regulate the change of form, consistently of course with the great law of conservation, and consistently also with the third

law, or that of the dissipation of energy. Grove in this country and Meyer on the continent have done good service in pointing out how the various forms of energy are correlated, and many of those philosophers who have been engaged with the conservation of energy, such as Joule, Helmholtz, Lord Kelvin, Rankine, &c., have necessarily advanced the subject; nevertheless, the complete laws which regulate the transmutation of the various kinds of energy into one another are as yet very imperfectly known. Rankine especially has given the laws of transmutation of energy in the most general form possible.

The third law, or that of the dissipation of energy, will be considered in a future part of this work.

322. Various forms of energy. Before concluding this chapter we will give a list of the various forms of energy, and state very briefly some of the more prominent transmutations from the one into the other. In the first place, all these forms may be divided into two classes:—

I. **VISIBLE OR MOLAR ENERGY**, or energy of motions and arrangements on the large scale.

II. **MOLECULAR AND ATOMIC ENERGY.**

In the first of these classes, under the head of visible energy we have—

A. *Molar kinetic energy*; that is to say, the energy of a body in visible motion.

B. *Potential energy of molar arrangement*; that is to say, a body in a position of advantage with regard to the force of gravity, the force of a spring, or any other force acting through large spaces. A head of water is a very good instance of this kind of energy, and every one is familiar with the work a head of water is capable of accomplishing.

In the class of molar energy we may embrace those vibrations of bodies which give rise to sound. A body in vibration is very similar to an oscillating pendulum, in

which case we have already seen (Art. 316) that the energy is alternately all kinetic and all potential.

In the class of invisible energy, embracing molecular and atomic energy we have—

C. *The energy of electricity in motion.* When a current of electricity passes along a wire, the wire will be heated to some extent, but if it be a very good conductor the heating effect will be comparatively small. In such a case we know that much more energy has passed through a given length of the wire than can be accounted for by the heating effect produced. This is the energy of electricity in motion.

D. *The energy of radiant heat and light.* This is a species of energy which is capable of passing through interplanetary space without sensible loss; it is also capable of passing through certain bodies with very little absorption.

We imagine radiant light and heat to consist of a vibratory motion of a certain kind of matter. The energy of this matter whose motions cause radiant light is therefore perhaps similar to that of a vibrating body or pendulum; that is to say, it is alternately all potential and all kinetic.

E. *The kinetic energy of absorbed heat.* When radiant heat and light are absorbed, or when a body becomes heated by any means, we have reason to believe that a great portion of the energy of this absorbed heat is transformed into a peculiar motion of the molecules of the body.

F. *Molecular potential energy.* Part of the absorbed heat is also spent in producing energy of expansion or separation of the molecules of matter against the force by which they are attracted to each other. It is thus spent in producing a species of potential energy, molecular attraction being the force in this case, just like gravity, or the force of a spring, in the case of the potential energy of visible motion. There are besides other forms of molecular potential energy.

G. There is also *the potential energy caused by electrical*

separation. Thus two separated spheres, one charged with positive and the other with negative electricity, attract each other. A position of advantage is thus obtained with respect to the force of electricity analogous to that which is obtained with respect to the force of gravity when a stone is separated from the earth.

H. There is also *the potential energy caused by chemical separation.* In the expansion produced by heat we have chiefly one molecule separated from another of the same body; but in chemical separation we have one element of a compound body separated from the other, and in this separation we have obtained a position of advantage with respect to that very powerful force known as chemical affinity.

It is not of course pretended that there may not prove to be some kind of energy which is not embraced in this list, or that no two of these varieties here given are reducible into one. The list is simply one of convenience.

323. Now with regard to these various forms of energy, the principle of the conservation of energy asserts that for a body left to itself, or for the entire material universe, we must have—

$$A + B + C + D + \&c. = \text{a constant quantity ;}$$

on the other hand, the various terms of the left-hand member of this equation must be considered as variable quantities, subject however to the above limitation, but capable of being transmuted into one another according to certain laws.

324. Laws of transmutations of energy. The following are amongst the most important cases of transmutation of these energies into one another :—

A, or molar kinetic energy, is transmuted into **B**, or the potential energy of molar motion, when a weight is projected

upwards above the earth ; into **C**, or electricity in motion (ultimately into heat), when a revolving conductor is brought between the poles of a powerful magnet.

As far as we know at present, **A** is not directly transmuted into **D**, or radiant light and heat ; it is transmuted into **E** and **F**, which embrace the energy, both kinetic and potential, of absorbed heat, when friction stops a body in motion and the body becomes heated in consequence ; into **G**, or the potential energy of electrical separation, in the machines which produce frictional electricity. The electrical separation produced makes it harder to drive the machine. **A** is possibly not converted directly into **H**, or chemical separation.

B, or the potential energy of molar motion, is generally converted first into **A**, or molar kinetic energy, and through it into other forms of energy. It is converted into **A** when a stone is rolled down a mountain, or when a head of water is made to drive a mill-wheel.

C, or the energy of electricity in motion, is converted into **A**, or visible kinetic energy, when two wires conveying electrical currents in the same direction attract each other ; a certain amount of the strength of the two currents is thus spent in producing the kinetic energy of the visible motion as they approach each other ; into **E** and **F**, or absorbed heat, when an electric current passes through a body which presents any resistance to its passage ; into **H**, or chemical separation, when a current of electricity is made to decompose a body.

D, or the energy of radiant light and heat, is converted into **E** and **F**, or absorbed heat, when radiant heat is absorbed by a body ; into **H**, or chemical separation, when a ray of sunlight decomposes chloride of silver.

E and **F**, or the energy (kinetic and potential) of absorbed heat, is converted into **A** and **B**, or the energy (kinetic and potential) of molar motion, in the case of any heat-engine ;

into **C**, or the energy of electricity in motion, in thermo-electric currents (Art. 163); into **D**, or radiant light and heat, when a hot body radiates, which it always does; into **G**, or electrical separation, when tourmalines and other crystals are heated (Art. 167); into **H**, or chemical separation, when a body is decomposed by heat.

G, or electrical separation, is transformed into **A**, or the kinetic energy of molar motion, when two bodies oppositely electrified approach each other; into **C**, or the energy of electricity in motion, when they are connected together by a wire or when a spark passes.

H, or the potential energy of chemical separation, is transmuted into **C**, or the energy of electricity in motion, when a voltaic battery of zinc and copper plates is in action; into **E** and **F**, or heat, when a body burns in air, or generally when chemical combination takes place; into **G**, or electrical separation, when two dissimilar metals are brought into contact.

325. These are some of the chief instances of transmutation of energy. In the remainder of this work we shall confine our attention to those transmutations in which the energy of heat embraced under the heads **D**, **E** and **F** is converted into other forms of energy, or in which other forms of energy are converted into heat.

CHAPTER II.

Relation between Heat and Mechanical Effect.

FIRST LAW OF THERMO-DYNAMICS.

326. ALLUSION has already been made to the experiments of Davy, in which ice was melted by the friction against

each other of two pieces of this substance; and also to those of Rumford, in which the friction of boring cannon was found to produce great heat, sufficient even to cause a considerable quantity of water to boil. The opinions of these philosophers were also quoted, in both of which it was distinctly stated that in friction motion is converted into heat. Motion is, in fact, *annihilated* as visible motion, while at the same instant heat is *created*. Visible motion is likewise converted into heat in certain cases of deformation, in compression, in percussive motion, and also in a vibrating body, in which the energy of vibration is ultimately converted into heat; but this transmutation can best be studied in the case of friction.

If, therefore, by means of friction, percussive motion, &c., there is a transmutation of mechanical energy into heat, it becomes an experimental question of great importance to ascertain how much mechanical energy is required to produce one unit of heat; or in other words, what is the relation between the unit of mechanical energy and the unit of heat; the latter unit being chosen as the amount of heat necessary to raise one kilogramme of water from 0°C to 1°C . We have, in fact, to inquire how far a kilogramme of water must fall under the influence of gravity in order to acquire mechanical energy by the fall which, when entirely converted into heat, will raise its temperature 1°C .

327. Joule's experiments. I. Fluid friction. This experimental question has been answered by Joule. His experiments began in 1843 and were continued until 1849. During this time he had learned to perfect his apparatus and to eliminate the various sources of error in such a manner that the results of different processes coincided in giving almost identical values for the mechanical equivalent of heat.

His experiments on the friction of fluids were conducted in the following manner. A known weight is attached to a pulley as in Fig. 72, the axle of this pulley resting upon friction rollers at f ; a string passing over the pulley is also wrapped round the roller r , so that by descent of the weight a rapid motion round a vertical axis is communicated to this roller.

This roller communicates its motion to a system of paddles placed in a fluid which fills the box B . A vertical

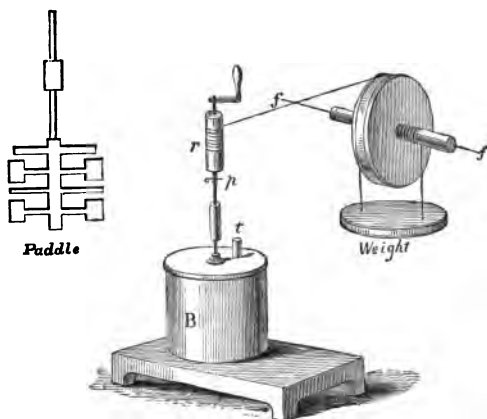


Fig. 72.

section of one of these paddles is given in the figure. There are eight sets of these revolving between four stationary vanes, which thus prevent the liquid from being whirled in the direction of rotation. The mechanical energy employed in producing the rotation was measured by the descent of a known weight through a known distance, and by undoing a small peg p the weight could be wound up again without moving the paddles in B . Great care was taken to correct for the amount of energy expended in

friction of the axles of the pulleys employed. In this experiment it is evident that the mechanical energy of the weight is expended in fluid friction in the box *B*, and by this means is ultimately converted into heat. A delicate thermometer at *t* gives the temperature with great exactness, and, the usual precautions being taken to eliminate the effects of radiation and conduction, it is evident that the amount of heating effect may be accurately measured, and by knowing the thermal capacity of the box and its contents this may ultimately be expressed in terms of the unit of heat. Joule also made experiments on the friction of iron. In these a disc of cast-iron was made to rotate against another disc of cast-iron pressed against it; the whole being immersed in a cast-iron vessel filled with mercury. By all these experiments it was found that the quantity of heat produced by the friction of bodies, whether solid or liquid, is always proportional to the quantity of work expended, and that the number of units of work in kilogrammètres necessary to raise by 1°C the temperature of one kilogramme of water taken at about 10°C was as follows:—

423.9	from friction of water, mean of 40 experiments.
424.6	„ mercury „ 50 „
425.2	„ cast-iron „ 20 „

In 1878 Dr. Joule repeated his experiments on the friction of water. The method he adopted was to revolve a paddle in a delicately supported vessel of water and to find the heat thereby produced, measuring the work by the force required to hold the vessel from turning and the distance run as referred to the point at which the force was applied; in other words, making use of the principle that the work transmitted by a shaft is equal to the moment of the force multiplied by the angle of rotation of the shaft.

He obtained from these experiments the value 423.9 for water at 16°.5C, which agrees extremely well with his previous results; but from a comparison of Joule's thermometer with a standard air-thermometer Professor Rowland has shewn that this value must be increased, and from a new comparison of this thermometer with the standard nitrogen-thermometer of the International Office Professor Schuster gives the result of Dr. Joule's experiments as 425.2 at 15°.

Experiments of a similar kind have been made by Professor Rowland (in 1880) and M. Miculescu (in 1892), and their results agree extremely well with that of Joule as thus corrected.

328. II. Electrical methods. Other methods were used by Joule; one of these took advantage of magneto-electricity, and was essentially the same experiment which was afterwards put in the following form by Foucault.

If a metallic disc or top in rapid rotation be brought between the poles of a powerful electro-magnet, induced currents will be generated in the top in consequence of its rotation in presence of the magnet, the tendency of which will be to bring the top to rest. The effect is exceedingly curious, and if it be asked what becomes of the energy of the rotation, the answer is that it is converted in the first place into electricity in motion, but ultimately into heat, and that in consequence the temperature of the disc will be found to have increased. If the disc be turned by hand the effect is very strange; it is found almost impossible to move it while the electro-magnet is in its neighbourhood, though when the current is broken it is exceedingly easy to do so. At the expense of much labour the disc, so revolving between the poles of the magnet, may be heated until it is too hot to be touched.

Another method was by estimating the energy converted

into heat by the passage of an electric current through a metallic wire. Very complete experiments after this method have been recently made by Mr. Griffiths and by Professor Schuster and Mr. Gannon, who have respectively obtained the values 428 and 427·8 kilogrammètres at Greenwich for water at 15°C.

329. III. Condensation of gases. Another method of deriving the mechanical equivalent of heat depends on the phenomena accompanying the condensation of gases. Many familiar experiments shew that when a gas is suddenly compressed there is a production of heat, and that when suddenly expanded there is an absorption of heat.

Séguin and Mayer had already suggested the use of gases and vapours for the purpose of determining the mechanical equivalent of heat; and air, the substance chosen by Mayer, was no doubt very good for such a purpose; nevertheless, the suggestions of these philosophers do not seem to have been accompanied with a clear appreciation of all the data necessary to a complete proof.

330. Joule, however, in his experiments supplied what was wanting in order to derive a good determination of the mechanical equivalent of heat from the known gaseous laws. By compressing air forcibly into a receiver surrounded by water he found that the water was considerably heated. It is not, however, correct to infer without further experiment that the amount of heat produced in this case is the exact equivalent of the energy expended in compressing the air. A familiar instance will make this clear. By a blow of a hammer upon a small quantity of fulminating mercury it is exploded and produces a considerable amount of heated gas, but we are not at liberty to suppose that all the heat thus developed is merely the mechanical equivalent of the energy of the blow, as will

be evident by supposing such an extreme case as a ton of the fulminating powder.

Evidently the substance is in different molecular conditions at the end of the experiment and at the beginning, and it may be supposed with much truth that the heat produced is nearly all due to the conversion into a kinetic form of a certain potential energy present in the compound. Now in the experiment above described, in which air is compressed, the air is evidently in a different molecular condition after compression, for the particles are much nearer together. The first thing therefore is to determine how much, if any, of the heat produced may be due to this change of the molecular condition of the air, and how much to the work expended in compressing the air.

331. The following very ingenious experiment performed by Joule is conclusive in shewing that the mere change of

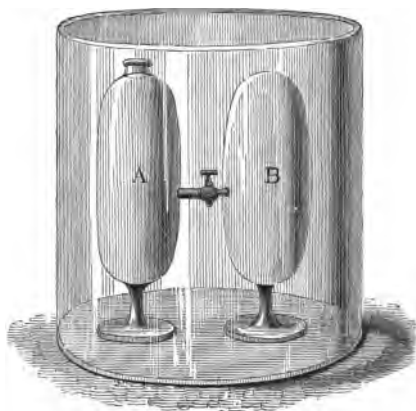


Fig. 73.

distance of the molecules of a permanent gas neither produces nor absorbs heat to an appreciable extent. In Fig.

73 we have two strong vessels, of which *A* contains compressed air, say under the pressure of 20 atmospheres; *B*, on the other hand, is a vacuum. The two vessels are connected with each other by a tube having a stop-cock which we may suppose to be shut. The whole apparatus is plunged into a vessel of water. After the temperature of the water has been very accurately ascertained, open the stop-cock, and thus allow both vessels to have the same pressure.

When the experiment is finished it will be found that there is no change in the temperature of the water. The prevalent idea is that when air expands it becomes colder, and that when condensed it becomes hotter; but Joule by this experiment has shewn that no appreciable change of temperature occurs when air is allowed to expand in such a manner as not to develop mechanical power. It follows as an inference that when air is compressed the rise of temperature is scarcely at all due to the mere diminution of the distance between the particles, but almost entirely to the mechanical effect which must be spent on the air before this condensation can be produced.

331 a. Mechanical equivalent of heat. From the results of experiments on fluid friction we may take 426 as the number of kilogrammètres necessary to raise one kilogramme of water through 1°C ; but strictly speaking, this determination is for the value of gravity at Greenwich and for water at 15°C . This work, 426 kilogrammètres, is generally called the *mechanical equivalent of heat*; it would be more correctly termed the *mechanical equivalent of the heat-unit*, and 426 may properly be said to be the mechanical value of the specific heat of water at 15°C .

332. Specific heat of gas of constant volume. In Arts. 297, 298 a distinction was made between the specific heat of a gas of constant volume and that of the

same gas of constant pressure, and the determinations therein exhibited were those of Regnault and Joly.

The determinations of the former give the specific heat of various gases under constant pressure; that is to say, when the gas remains at the same pressure during the various temperatures to which it is exposed.

Dr. Joly shewed how we may experimentally find the specific heat of a gas of constant volume; nevertheless, before his experiments, this specific heat was obtained from the other without trouble by means of the knowledge derived from the experiments of Joule.

Thus let us consider a rectangular prismatic vessel one square mètre in section (Fig. 74), and suppose that we have a cubic mètre of air under the ordinary pressure of 760 millimètres of mercury reduced to 0°C contained in it, the temperature of the air being also 0°C . The whole force on the surface aa , which shuts in this air, may easily be found; it will in fact be the weight of a column of mercury whose base is one square mètre and whose height is 0.760 metre. Now the specific gravity of mercury at 0°C is 13.596 (Art. 75),

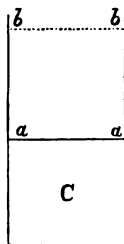


Fig. 74.

that is to say, a cubic décimètre (or .001 of a cubic mètre) of mercury at 0°C will weigh 13.596 kilogrammes, and hence the above column of mercury will weigh $760 \times 13.596 = 10333$ kilogrammes nearly. We may suppose, for the sake of simplicity, that there is no atmosphere above this air, and that it is kept down by a veritable weight of 10333 kilogrammes above it. The mass of this cubic mètre of air will at 0°C be (Art. 149) 1.2932 kilogrammes nearly, and if it be raised in temperature through an interval of $100 \div 0.3670 = 272^{\circ}.4\text{ C}$ its volume under the same pressure will be (Art. 64)

exactly doubled ; that is to say, it will have raised the weight of 10333 kilogrammes one mètre high and done work represented by 10333 kilogrammètres.

Now according to Regnault's determination, Art. 299, the specific heat of air is 0.237 ; that is to say, only 0.237 of the amount of heat necessary to raise a kilogramme of water one degree in temperature will be required in order to raise a kilogramme of air under constant pressure one degree in temperature.

Hence the amount of heat necessary to raise this air from 0°C to 272.4°C under constant pressure will be—

$$1.2932 \times 0.237 \times 272.4 = 83.51 \text{ heat units.}$$

In this expression the first factor refers to the mass of the air, the second to its specific heat, and the third to its increase of temperature. But in the course of this increase of temperature work equal to 10333 mechanical units, or (Art. 331 a) $10333 \div 426 = 24.26$ heat units, has been done.

Hence, of all the heat expended upon this air, or 83.51 units, 24.26 units have been spent in work. Hence also $83.51 - 24.26$ or 59.25 units denote the amount of heat consumed in the mere heating of the particles.

But, according to Joule's experiment, if the air had throughout been confined to one cubic mètre, and afterwards made to occupy two cubic mètres without doing any work, the whole heat of the particles would be the same in the second case as in the first. But we have seen that the mere heat consumed in heating the particles occupying the two cubic mètres is 59.25 units ; hence this also will represent the heat required to raise the air remaining at the constant volume of one cubic mètre through 272.4°C. It thus appears that if 83.51 be used to represent the specific heat of this air under constant pressure, 59.25 will represent its specific heat at constant volume.

According, therefore, to our usual method of measuring specific heat, $0.237 \times \frac{59.25}{83.51} = 0.168$ will denote the specific heat of air, the volume of which remains constant during experiment.

SECOND LAW OF THERMO-DYNAMICS.

333. Reversible engines. Having now described at some length the first law of thermo-dynamics and the experimental proofs of the same, let us proceed to consider the second law, which relates to the conversion of heat into work.

The following proof of this law is deduced from that given by Lord Kelvin.

In establishing this very important principle recourse is had to a conception of Carnot, to whom this branch of science is much indebted, although his idea of the nature of heat was erroneous.

This conception is that of an engine completely reversible in all its physical and mechanical agencies. Such an engine must be supposed to have a source of heat and also a refrigerator, the temperature of the first being of course higher than that of the second, and it produces work while it transfers heat from the source to the refrigerator. If worked forwards, such an engine will produce a certain amount of work from a certain amount of heat which leaves the source ; but if worked backwards, owing to its perfect reversibility, it will, at the expense of the same amount of work, bring back the same amount of heat into the source.

334. Now it may easily be shewn that a perfectly reversible engine will produce as much mechanical effect as can be produced by any heat engine, with the same temperatures of source and refrigerator, from a given quantity of heat. For let there be two heat engines *A* and *B*, of which

B is a reversible engine, both working between the same temperatures, and if possible let A derive more work from a given quantity of heat than B . Now if A be worked forwards, a quantity of work W is produced by it during the conveyance of a quantity of heat Q from the source of heat.

If B were worked forwards, a quantity of work w (less than W by hypothesis) would be derived from the same quantity of heat Q ; but, since B is completely reversible, if worked backwards it would restore to the source of heat a quantity of heat Q by the expenditure of a certain amount of work w (less than W).

Thus we have—

A working forwards and producing an amount of work W by carrying heat $= Q$ from the source.

B working backwards and spending an amount of work w (less than W) in order to carry heat $= Q$ to the source of heat.

But, since the work produced by A is greater than that spent by B , A may be made to work B , and hence the whole arrangement becomes self-acting; while, on the whole, the source neither gains nor loses heat, and work equal to $W - w$ is produced during each double cycle of operations. Now, as far as this problem is concerned, we may suppose all the bodies surrounding the source (with the exception of the refrigerator) to be of the same temperature as the source, and therefore, if the hypothesis with which we started is correct, we may go on continually producing work by the mere presence of a refrigerator, or body of lower temperature; while, at the same time, no heat is conveyed from the bodies of higher temperature which are supposed to surround this refrigerator.

Since however, consistently with the conservation of energy, heat must disappear *as heat* in order to produce this work, we see that this heat must in this supposed case

really come from the body of low temperature; that is to say, work is produced by abstracting heat from a body of already low temperature. A little reflection will shew that such a process might be carried on for ever, and would result in a perpetual motion; but since we cannot admit the possibility of such a case, we are forced to conclude that our hypothesis is erroneous.

But our hypothesis was, that of two engines A and B , of which the latter is reversible, working between the same source and refrigerator, A could produce more work than B out of the same quantity of heat. We are thus driven to the conclusion that under similar circumstances B produces as much work as A ; and therefore that the test of maximum work under given circumstances is *reversibility*.

335. Reversible engines of infinitely small range.

In the next place let us take a mass of any substance (for the sake of simplicity we may suppose it to be fluid), and let its surface be subjected to the uniform pressure p ; also let its volume be v while its temperature is t .

Let us imagine this substance to form our heat engine; that is to say, let us imagine certain operations at different temperatures to be performed on this substance whose result is that heat is transmuted into work.

And here it is well to observe that we need not trouble ourselves about the practicability of making such an engine; all that we need care about is that our conception is precise and mechanically conceivable.

Let us reckon pressures and volumes along two axes at right angles to one another as in Fig. 75, and let us suppose our substance to have a volume v denoted by og , its pressure p being represented by ga . Now, in the first place, let it expand from volume v to $v + dv$, its temperature being kept constantly t ; at the end of this expansion its volume may be supposed to be oi and its pressure ib ,

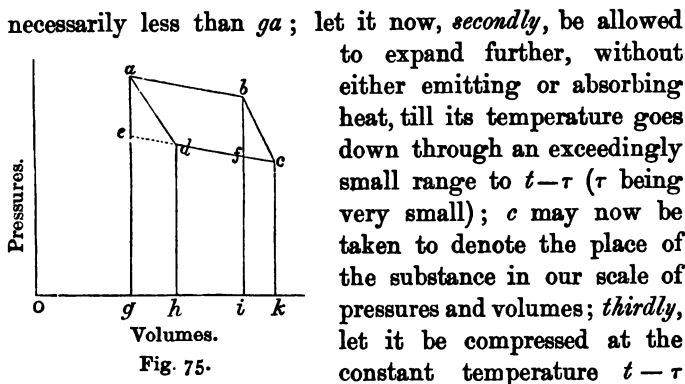


Fig. 75.

(differing infinitely little from t) so much that when, *fourthly*, the volume is further diminished to the original volume v without the substance being allowed either to emit or absorb heat, its temperature may be t .

336. Here, then, we have first of all two expansions, and next two similar compressions bringing back the body to its original state, and the first compression is the reverse of the first expansion, while the second compression is the reverse of the second expansion, and all are supposed to be extremely small.

Evidently, therefore, the line which denotes the first compression will be parallel but opposite in direction to that which denotes the first expansion, and the same will hold for the other two lines; so that, provided all the movements be sufficiently small, the four positions of the body will be the four corners of a parallelogram $abcd$. Now the work done by the body during the expansion between a and b (equal to the product of the mean pressure on its surface and the change of volume) will be denoted by the area $abig$, also that done by the body between b and c will be denoted by the area $bcki$. Hence the whole work done by the body between a and c will be denoted by the area $abckg$.

In like manner the work performed AGAINST the body during the compression between c and d will be the area $ckhd$, and that done against the body by the further compression between d and a will be the area $dhga$. Hence the whole area $ckgad$ will denote the whole work done AGAINST the body.

Now the difference between the area $abckg$, or the work done by the body, and the area $ckgad$, or the work done against the body, is the parallelogram $abcd$.

Hence this parallelogram denotes the whole surplus work done BY the body in its cycle of operations.

337. In the next place, the whole heat abstracted from the source of higher temperature t is that required to heat the body as it increases in volume from v to $v + dv$, this operation being performed at the temperature t , while, on the other hand, when the body is finally restored to this temperature t it has only the volume v .

Heat corresponding to the volume $v + dv$ is therefore taken from source t , while heat corresponding to the volume v is restored to this source.

Hence the whole heat abstracted from source t is that required to increase the volume of the body at the constant temperature t from v to $v + dv$.

This may be called Mdv .

338. Let us now suppose the cycle of operations to be reversed, or the engine to be worked backwards starting from c and from the lower temperature $t - \tau$.

First, let the body contract in volume without giving or receiving heat until it becomes of the temperature t .

Next, let it be further contracted at the constant temperature t through the volume dv .

Thirdly, let it expand without giving or receiving heat till it falls to the temperature $t - \tau$. And

Fourthly, let it expand at the constant temperature $t - \tau$ through the volume dv .

It will be seen that in this cycle the body goes from c to b and from b to a having *work done UPON it*; while it goes from a to d and from d to c having *work done BY it*.

The *work done UPON it* is represented therefore by the larger area $abckg$, and *that done BY it* by the smaller area $ckgad$; and on the whole there is a surplus of *work done UPON the body* denoted by the parallelogram $abcd$. At the same time it will be noticed that in the second operation, where the body is contracted from $v + dv$ to v (going from b to a) at the temperature t , there is a surplus supply of heat brought to the source equal to Mdv .

339. Thus when this engine was worked in a direct manner we had *work produced* equal to the area $abcd$, while heat was *drawn from the source* equal to Mdv . Now when the engine is reversed we have *work spent* equal to the same area $abcd$; while heat is *brought to the source* equal as before to Mdv . A body acted upon in this manner forms therefore a reversible engine, and we are entitled to apply to it the reasoning of Art. 334, and to conclude that, whatever be the substance employed between the limits of temperature t and $t - \tau$, if the heat drawn from the source or Mdv remain constant, the work done, or the area $abcd$, will also remain constant; in other words, for the same temperature-limits the ratio between Mdv and the area $abcd$, or $\frac{M dv}{\text{area } abcd}$, is constant, whatever be the substance used.

340. The area $abcd$ is easily found thus:—

Produce cd to cut ag in e . Now area $abcd = \text{area } abfe$, since they are on the same base and between the same parallels; but area $abfe = ea \times \text{perpendicular distance between } ea \text{ and } fb = ea \times gi$. Hence area $abcd = ea \times gi$.

Now if the operation denoted by the body going from c to d , namely the contraction of volume at the fixed temperature $t - \tau$, be continued until the original volume v is reached,

that is, up to the line ga which limits this volume, we should be brought to the point e ; ge would thus denote the pressure of the body at temperature $t - \tau$ and at volume v ; while ga is the pressure at the same volume but at temperature t .

Hence ae denotes the change of pressure of the body at constant volume v while the temperature falls from t to $t - \tau$. If we consider the pressure to be a function of the temperature t and the volume v , ea will thus be represented by $\frac{\partial p}{\partial t} \tau$; that is to say, by the partial differential coefficient of this function with respect to t when v is constant multiplied by the small temperature-change τ . Again, gi is evidently the change of volume or dv . Hence—

$$\text{Area } abcd = ea \times gi = \frac{\partial p}{\partial t} \tau dv.$$

341. Carnot's function. Hence also

$$\frac{M dv}{\text{area } abcd} = \frac{M dv}{\frac{\partial p}{\partial t} \tau dv} = \frac{M}{\frac{\partial p}{\partial t} \tau};$$

and this ratio is constant for the same temperature t and range τ whatever be the substance used: but if in going from one substance to another we always adhere to the same value of τ , or keep the fall of temperature the same, it will thus become a constant multiplier, and we may therefore dispense with it and assert that $\frac{M}{\frac{\partial p}{\partial t}}$ is constant for the same

temperature whatever be the substance used. In other words, $\frac{M}{\frac{\partial p}{\partial t}} = \phi(t)$; that is to say, it is a function of the

temperature only, and does not vary with the nature of the substance.

This very important common property of all bodies was first discovered by Carnot.

342. Probable form of this function. Since therefore this function is the same for all substances, in order to determine its form let us take some one body whose laws are best known. Let us, for instance, take a perfect gas, and consider in the first place the relation which subsists between the temperature and pressure of such a gas whose volume is v . This is very easily found, for if P denote the pressure of this gas at 0°C , its pressure at t° will (Art. 63) be $P(1 + at)$.

Now we have reason to conclude from the experiment of Joule (Art. 331) that the molecular heat of the particles of a perfect gas whose temperature is constant is independent of the volume of this gas, being the same for a great volume as for a small one. The heat absorbed when such a gas expands at a constant temperature is therefore the exact equivalent of the work done in expansion.

Hence the mechanical equivalent of Mdv , that is to say, of the heat absorbed while the gas increases in volume at the constant temperature t from v to $v + dv$, will be denoted by the work done, that is, by $p dv$ or $P(1 + at)dv$.

Hence if we use J to denote the multiplier by which our heat-unit must be multiplied in order to produce the mechanical equivalent (that is to say, $J = 426$ (Art. 331 a)), we shall have—

$$JMdv = P(1 + at)dv; \quad \therefore M = \frac{P(1 + at)}{J}.$$

But again, since $p = P(1 + at)$, we have $\frac{\partial p}{\partial t} = Pa$; and

$$\text{hence} \quad \frac{M}{\frac{\partial p}{\partial t}} = \frac{P(1 + at)}{JPa} = \frac{1 + at}{Ja}. \quad (1)$$

343. This therefore is most probably the true value of

the function $\phi(t)$, and the expression may be rendered yet simpler by the following assumption.

Instead of considering 0°C as our zero of temperature, let us, while adhering to centigrade *degrees*, take a different zero to start from. Let this zero be such that our new temperature shall be proportional to $(1 + at)$, so that, if the ratio of this proportion be some number m , we shall have

$$\text{New temperature} = m(1 + at).$$

Hence at 0°C we shall have new temperature or $T_0 = m$;

and at 1°C " " $T_0 + 1 = m(1 + a).$

Subtracting the upper expression from the lower, and putting $a = .003665$ (Art. 63), we find—

$$1 = am; \quad \therefore m = \frac{1}{a} = \frac{1}{.003665} = 273 \text{ nearly.}$$

Hence at 0°C $T_0 = 273^\circ$ according to our new notation, and generally—

$$\text{New temp.} = \frac{1}{a}(1 + at^\circ\text{C}) = \frac{1}{a} + t^\circ\text{C or } t^\circ\text{C} = \text{new temp.} - \frac{1}{a}.$$

Making this substitution in (1), we have—

$$\frac{M}{\frac{\partial p}{\partial t}} = \frac{1 + a \left(\text{new temp.} - \frac{1}{a} \right)}{Ja} = \frac{\text{new temp.}}{J}. \quad (2)$$

This new temperature is generally called *absolute temperature on the air-thermometer*.

344. Perfect engines of great range. We have hitherto confined our observations to a perfect engine working through an infinitely small temperature-range; let us now attempt to find how much work will be produced from a given quantity of heat by an engine working between a source of temperature T_s and a refrigerator of temperature T_R , according to the new scale of temperature just mentioned. In discussing this problem let us (adopting the

words of Lord Kelvin) suppose the great engine to consist of, or to be broken up into, an infinite number of perfect engines, each working within an infinitely small range of temperature and arranged in a series of which the source of the first is the given source, the refrigerator of the last the given refrigerator; while the refrigerator of each intermediate engine is the source of that which follows it in the series. In order to make this reasoning perfectly clear we may follow out the analogy suggested by Carnot, in which he compares the mechanical energy derived by carrying heat from a body of a higher to one of a lower temperature to the mechanical energy of water falling from a higher to a lower level. The imaginary breaking up of the great engine into an infinite number of small engines is thus analogous to the breaking up a great waterfall into a vast number of very small stages. But we must not pursue the analogy too far.

Now each of these small engines will in any time emit less heat to its refrigerator than is supplied to it from its source by the amount which represents the mechanical work which it produces. Now let q denote the quantity of heat which such an intermediate engine discharges into its refrigerator in any time, while $q + dq$ denotes the quantity which it draws from its source in the same time; also let t and $t + dt$ denote the temperatures (on the new scale) of the refrigerator and source of this intermediate engine.

345. Denoting as before by J the mechanical equivalent of unit of heat, then the work done by this small intermediate engine in the given time will be equal to

$$Jdq. \quad (3)$$

But since dt replaces τ of Art. 335—that is to say, since it denotes the difference of temperature between the source and refrigerator of our small engine—we shall have the following proportion:—

Work done: heat drawn from source (or q) :: $\frac{\partial p}{\partial t} dt dv : M dv$.

Hence—

$$\text{Work done} = \frac{q}{M} \times \frac{\partial p}{\partial t} dt = q \times \frac{J dt}{t} \text{ (Art. 343).} \quad (4)$$

Now since (3) and (4) are Both different expressions for the work done, we may equate them together. Hence we have—

$$J dq = J q \frac{dt}{t}; \text{ and hence } \frac{dq}{q} = \frac{dt}{t}. \quad (5)$$

Let us now, in Fig. 76, represent the temperatures (t) (new scale) of the various intermediate engines by lines of abscissæ starting from the origin O ; while we raise ordinates to denote the whole quantity of heat (q) that has passed during the time under consideration through an intermediate engine of temperature t denoted by the corresponding abscissa; and

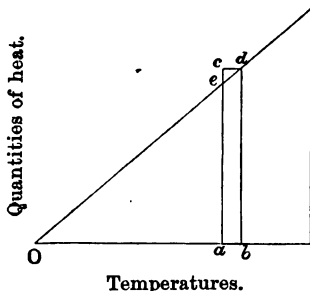


Fig. 76.

let us join the extremities of these ordinates so as to form a line. It is very easy to shew that this line will be a straight line. For $ae = q$ and $ec = dq$, also $Oa = t$, $ab = dt$. Now if Oed be a straight line, we have—

$$ec : ae :: ed : Oe :: ab : Oa;$$

that is to say—

$$dq : q :: dt : t; \text{ or } \frac{dq}{q} = \frac{dt}{t}.$$

The condition (5) is therefore fulfilled by a straight line of this description; and indeed we may arrive at the same result by a direct integration of (5).

346. Work done by perfect engines. Having thus

determined that the line *Oed* is a straight line, the work done by the great engine can be very easily found; for let T_s and T_R be the temperatures (new scale) of the source and refrigerator of this great engine, while Q_s is the quantity of heat which passes from its source, and Q_R is the quantity of heat which passes through its refrigerator in a given time. Q_s and Q_R are thus ordinates of Fig. 76, while T_s and T_R are the corresponding abscissæ; and we have, since *Oed* is a straight line—

$$Q_R : Q_s :: T_R : T_s; \quad \therefore Q_R = Q_s \frac{T_R}{T_s}.$$

Also—
$$Q_s - Q_R = \frac{Q_s(T_s - T_R)}{T_s}.$$

But since during a given time while the given quantity of heat Q_s leaves the source it is only the smaller quantity Q_R which reaches the refrigerator, it is evident from the principle of the conservation of energy that the difference, or $Q_s - Q_R$, must have been transmuted into mechanical effect. Hence

$$J(Q_s - Q_R) = \frac{JQ_s(T_s - T_R)}{T_s} \quad (A)$$

is the quantity of work produced by the engine in this time; that is to say, this expression represents the amount of work produced by a perfect engine working between temperatures T_s and T_R (new scale) during the time that a quantity of heat $= Q_s$ is conveyed from the source. It is unnecessary to notice the importance of this result in the theory of steam engines and of heat engines in general.

It is very easy to illustrate this conclusion by means of a numerical example. Let us conceive, for the sake of simplicity, an air engine working at a very low temperature and with a very small difference between the source of heat and the refrigerator. Let the source be of the temperature 0°C , or according to the notation just in-

troduced 273° , while the refrigerator is $0^{\circ}\cdot 1\text{C}$ lower or $272\cdot 9$. Let us also suppose that we have a cylinder filled with air, of which the cross section is one square mètre; also let the force exerted upon the piston be 2160 kilogrammes' weight. Suppose now, for the sake of simplicity, that the contents of the cylinder are 2159 cubic mètres, and in the first place let the piston rise one mètre high, the temperature remaining the same. The air in the cylinder will now occupy 2160 cubic mètres, and the pressure on the cylinder, which varies inversely as the volume of the air, will now be 2159 kilogrammes' weight per square mètre, so that the mean force overcome during the rise of the piston may be taken as 2159.5 kilogrammes' weight; and since the piston was raised one mètre in height, work has therefore been done by the air during this operation equal to 2159.5 kilogrammètres. Now we know by Art. 331 that no internal work has been done in separating the particles of air from one another, and since the particles themselves are of the same temperature as before, the only expenditure of energy has been that required to lift the piston, so that 2159.5 kilogrammètres must represent the energy of the amount of heat of 273° temperature required for this expansion. This is the first operation of Art. 335; the next is to allow the air to expand farther, without either giving out or receiving heat, until the temperature falls through $0^{\circ}\cdot 1\text{C}$. Now we know both by experiment and calculation that in order to produce this fall of temperature the piston must rise 1.9405 mètres more, and hence the pressure at the end of the rise will have fallen, both on account of the increase of volume and the diminution of temperature. It will now have become

$$2159 \times \frac{2160}{2161\cdot 9405} \times \frac{272\cdot 9}{273} = 2156\cdot 272$$

units, and the mean pressure during the ascent may

therefore be taken as 2157·636 units, while the work done will have been $2157·636 \times 1·9405 = 4186·814$ kilogram-mètres.

Let us now proceed to the reverse operation and condense the gas. The air has now the temperature $272^{\circ}·9$, the pressure 2156·272 units, and the volume 2161·9405 cubic mètres; let it now be suffered to contract at this constant temperature through 1·0009 mètre. At the end of this contraction its pressure will have become

$$2156·272 \times \frac{2161·9405}{2160·9396} = 2157·271$$

units, and the mean pressure during the operation may be taken as 2156·772 units, and the work done upon the air will have been 2158·709 kilogrammètres. In the next and last stage let the air still contract, neither receiving heat nor giving it out through the remaining 1·9396 mètres, until when at the end it will be found to have regained at once its original volume, temperature, and pressure. Its mean pressure through this contraction will therefore be 2158·636 units, and the work done upon the air will be $2158·636 \times 1·9396 = 4186·814$ kilogrammètres. Let us here pause a moment and sum up what has been done. *Firstly*, the air was allowed to expand for one mètre at the temperature of 273° , doing work against the pressure equal to 2159·5 kgm. *Secondly*, it was further allowed to expand, neither receiving heat nor giving it out, until its temperature fell to $272^{\circ}·9$. During this expansion work was done by it against the pressure equal to 4186·814 kgm. So that in both expansions work was done by the air equal to 6346·314 kgm. *Thirdly*, the gas was made to contract one mètre at the temperature of $272^{\circ}·9$, work being done upon it by the pressure equal to 2158·709 kgm. *Lastly*, it was allowed to contract, without giving or receiving heat, until it reached its original volume, temperature,

and pressure, during which process work was done upon it equal to 4186.814 kgm., while during both contractions work was done upon it equal to 6345.523 kgm. The engine is now ready to start afresh, and during this cycle of operations there has been more work *done* by the air than *done upon* the air, yielding us a surplus available for external purposes equal to $6346.314 - 6345.523 = 0.791$ kgm. It is worthy of remark that this difference takes place entirely between the first and the third operations.

If we now consider our first operation we shall find that in order to produce this result we have taken a quantity of heat from the higher temperature equal to 2159.5 kilogrammètres. If we consider the other operations we shall also find that heat equal to 2158.709 kilogrammètres has been given out at the lower temperature, so that there has been a carriage of heat from the higher to the lower temperature equal to 2158.709 kilogrammètres, during which operation an amount of available work equal to 0.791 kgm. has been obtained, so that as nearly as possible $\frac{1}{2730}$ of the whole heat taken from the source of heat has been utilized.

Let us now vary the conditions, and suppose the source of heat to be of the temperature of boiling water, or (on the new scale) 373° , while the fall of temperature is $\frac{1}{10}$ of a degree centigrade as before. Taking as before the four operations necessary to a complete cycle, we have—

1. An expansion for one mètre—work done = 2159.5 kgm.

2. It is known that in order to produce a temperature fall of $\frac{1}{10}$ of a degree centigrade on the gas at this temperature it must be expanded through 1.42 mètres. The pressure at the end of this operation will be

$2159 \times \frac{2160}{2161.42} \times \frac{372.9}{373} = 2157$ kilogrammes' weight per square mètre, and the mean pressure during the expansion

will be 2158 units. Hence the work done will be $2158 \times 1.42 = 3064.36$ kgm. Hence also, the whole work done by the air during both expansions will be 5223.86 kgm.

3. The first contraction will be 1.00066 mètré and will have for its extreme pressures 2157 and 2158 units. Hence the work done upon the air will be 2158.921 kgm.

4. The second contraction will begin with the pressure 2158 units, and end with the original pressure 2160 units. Thus a contraction of 1.41934 mètrés will be gone through under an average pressure of 2159 units, and the work done upon the air will be 3064.36 kgm. Hence the whole work done upon the air during both contractions will be 5223.281 kgm. It will be found, as in the previous instance, that we have gained an amount of available work equal to $5223.860 - 5223.281 = 0.579$ kgm., while the heat taken from the source has been 2159.5 kgm., and we have therefore utilized as nearly as possible $\frac{1}{3730}$ of the whole.

We thus see that when the temperature of the source on the new scale is 273° and the temperature fall $0^\circ.1$, we realize a proportion of the whole heat taken from the source equal to $\frac{1}{3730}$, and also that when the temperature of the source is 373° and the temperature fall $0^\circ.1$ as before, the proportion realized is only $\frac{1}{3730}$.

These results are thus quite in conformity with the conclusions at which we have arrived by our analytical investigation.

347. Absolute zero of temperature. One peculiarity of the expression (A) remains to be remarked. If $T_R = 0$, then the work produced is JQ_S ; that is to say, all the heat Q_S which leaves the source is converted into work. Since we cannot possibly have more work than this from this quantity of heat, we are therefore precluded from supposing that T_R may be a negative quantity; that is to say, it

would seem that on this scale there can be no negative temperature or it would seem that the zero of this scale is the absolute zero of temperature. We shall return to the subject of the absolute zero of temperature.

CHAPTER III.

History of Heat Engines.

348. In the last chapter heat engines were discussed, but rather from a theoretical than a practical point of view.

A mechanically conceivable but nevertheless unattainable machine called a perfect engine was there imagined, and it was shewn that such an engine, having given temperatures of source and refrigerator, is only able to convert into mechanical effect, or utilize, a certain definite proportion of the heat which leaves its source. Also, the principles of the process by which heat is converted into work in such engines were given; so that by knowing the temperatures of source and refrigerator of a perfect engine the proportion of heat utilized can be at once ascertained.

But in practice engines are not perfect, and by no means produce the greatest possible amount of work which perfect engines of the same temperatures of source and refrigerator are capable of producing, although of late years the efficiency of heat engines has been very greatly increased.

Such machines also have hitherto been worked almost exclusively by steam, so that the history of heat engines is in fact that of the steam engine.

This history is one of great interest, and it is extremely instructive to trace the attempts to make use of steam from

their infancy to our own day, in which the steam engine plays so very prominent a part.

349. Hero's engine. In giving a short sketch of the history of the steam engine we may with much propriety limit ourselves to those attempts to produce by means of steam some motion of a useful kind which have been either made or at least suggested; and in this sketch the first engine which we shall have to describe is the Eolipyle of Hero of Alexandria, who flourished about 120 B.C.

This machine is represented in Fig. 77.

The principle of it is obvious, and is founded upon that law of motion which asserts that all action has an equal and contrary reaction as far as momentum is concerned. Thus when a musket is discharged the equivalent to the forward momentum of the ball and ignited gas is the recoil of the gun barrel, but the mass of the latter being much greater the velocity is of course much smaller.

In like manner when a rocket is ignited the reaction to the down rush of gas is the upward flight of the rocket.

The same principle applies to Hero's Eolipyle, which

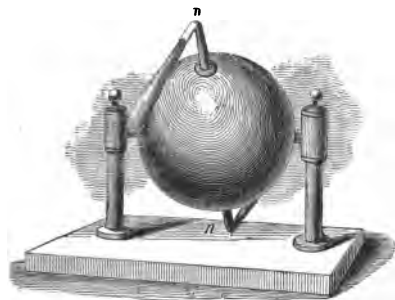


Fig. 77.

consists of a globe having two nozzles with narrow apertures, as in Fig. 77. This globe contains a quantity of water, which is made to boil by the application of a lamp (not shewn in the figure). As the heat is applied the vapour is forcibly discharged

through the nozzles; these nozzles may therefore be

compared to musket barrels; so that at each nozzle there is a recoil which is the exact equivalent of the momentum of the issuing steam. This recoil will not however be momentary but continuous, since the issue of the steam is continuous. Now the nozzles are so arranged that these forces of recoil form a couple, tending to produce a rapid motion of rotation of the globe about its axis.

350. Blasco de Garay. Passing over the Middle Ages, it is said that in the year 1543 Blasco de Garay, who was in the service of Charles V of Spain, succeeded in applying the motive power of steam so as to propel a ship of 200 tons burthen in the harbour of Barcelona at the rate of three miles an hour. This, if well authenticated, is a very extraordinary fact.

351. Porta, De Caus, and Worcester. J. B. Porta (1580), Solomon de Caus (1615), and the Marquis of Worcester (1663) appear to have independently conceived an application of steam of a kind somewhat like the following.

Our readers are no doubt familiar with an accident that sometimes happens with a common kettle if the lid be too tight and the level of the water be above the orifice of the spout; the pressure of the steam formed acts upon the surface of the water so as to drive it out at the mouth of the spout.

Now it seems to have been contemplated by these three inventors independently that the pressure of steam might thus be employed to raise a column of water, and by this means to do work; but it seems very doubtful if these conceptions ever led to the construction of a machine of any magnitude.

352. Papin. In 1690 Dr. Papin, a Frenchman, whose name we have already mentioned (Art. 123), conceived the idea of applying the motive force of steam to raise a piston,

while its descent might be effected by the condensation of the steam creating a vacuum.

For a long time it was thought that Papin did not carry his project into execution on a scale of any magnitude, but a correspondence has recently come to light which appears to shew that Papin not only conceived the idea of such a machine, but had this idea carried into effect. If we presume this to be the case, a very high rank must be given to Papin in the history of the steam engine.

353. Savery. In the year 1698 Captain Savery took out a patent for an engine for the purpose of raising water from mines.

The machine of Captain Savery was in reality a lift and force pump worked by means of steam. In the lift and force pump two operations are performed. In the first place, by the ascent of a piston a vacuum is formed in a chamber from which a pipe proceeds down to the reservoir of water, beneath the surface of which the extremity of this pipe is plunged. On account of this vacuum the external pressure of the atmosphere on the reservoir forces the water up this pipe, and ultimately into the chamber of the pump; while a valve opening upwards prevents it from returning.

The piston has, however, another office to perform: it drives the water out of the body of the pump into a side pipe, which it is thus forced to ascend, its descent being prevented as before by a valve.

Now in Savery's engine a receiver communicating by means of a pipe with the reservoir of water was filled with steam. The supply of steam was then shut off, and the steam condensed by means of a jet of cold water;—a vacuum was thus formed, and the external pressure of the air on the surface of the reservoir forced the water up the pipe into the receiver, its return being prevented by means of

a valve. When the receiver was thus nearly filled with water a communication with the boiler was again opened, and the pressure of the steam upon the water forced it up a pipe to a height determined by this pressure, its return being prevented by a valve.

The defects of this engine of Savery's are very manifest, and it was never extensively used: one great disadvantage was that the height to which water could be raised by this engine was dependent on the pressure of steam in the boiler; so that to carry water any considerable height an enormous pressure would be required.

354. Newcomen. Newcomen & Cawley conceived in 1705 the same idea that had previously occurred to Papin, namely, to make use of steam to move a piston. It is evident that if by an arrangement of this kind a considerable pressure is exerted on a piston of considerable area, and that if this piston is made to move through a considerable space, a great amount of useful work may be done.

In Newcomen's engine as finally constructed we may imagine the piston to be at the top of the cylinder, while the cylinder itself is filled with steam; the communication with the boiler is now cut off, while at the same time a jet of cold water made to play in the cylinder condenses the steam.

A vacuum is thus formed, and the pressure of the air upon the upper surface of the piston pushes it down with great force:—in descending the piston is made to perform useful work. When the piston has reached the bottom of the cylinder the communication with the boiler is again opened, the atmospheric pressure is thus balanced, and the machine itself by a simple arrangement is made to pull the piston up to the top of the cylinder.

When the piston has arrived at the top the communication with the boiler is once more cut off, the steam condensed, a vacuum formed, and the external pressure of the

air made to force the piston down, performing as before useful work in its descent, and so on again. It will be seen that this is in reality an atmospheric engine, and though in many respects objectionable, it was a form of engine that continued in use until the time of Watt.

355. Watt. Separate condensation. In the year 1763 James Watt, philosophical instrument maker to the University of Glasgow, was appointed to repair a model of a Newcomen engine that was used by the Professor of Natural Philosophy. He soon perceived the disadvantages attending the construction of this engine, and was led, after laborious study and much opposition, to realise certain improvements of the steam engine which have immortalised his name.

Watt perceived that in order for the piston of such an engine to descend with force it is necessary that there should be little pressure of steam opposed to that of the atmosphere, and hence that the cylinder, previously filled with steam, must be cooled, so as to condense the steam. But before another down stroke takes place it is necessary that this very same cylinder should be filled with steam of the ordinary atmospheric pressure, and hence that the cylinder should be hot.

It is, therefore, essential to this arrangement that the same cylinder should be heated and cooled alternately; but this produces a great waste of heat, and it soon occurred to Watt that the condensation might be performed in a separate vessel. In fact, the observations of Watt had led him to the result that we have stated in a previous part of this work (Art. 116), namely, that if vapour of water be introduced into two communicating vessels of different temperatures the pressure of the vapour will soon fall so as to correspond as nearly as possible with that due to the inferior temperature.

Watt's idea was therefore to keep the cylinder always as hot as possible, and when it was wished to condense the steam, to open up a communication between the cylinder and a separate chamber kept cold by the constant injection of water. By this means a vacuum might readily be made without the necessity of cooling down the cylinder.

This arrangement of separate condensation must be regarded as one of the greatest of Watt's discoveries, for by means of it, instead of alternately heating and cooling the same cylinder, the cylinder was always kept as hot as possible and the condenser always as cold as possible.

356. Air-pump. Another improvement was the air-pump. Watt saw that this water of injection would soon get heated, and that by its means also atmospheric air might be carried into the condenser. The usefulness of this separate chamber would thus be greatly impaired unless some arrangement were made for pumping out the heated water and the air.

This was done by an air-pump driven by the engine itself; and in order to economise heat as much as possible the boiler was fed by means of this heated water.

357. Double action. Another improvement of Watt was to transform the atmospheric engine into a steam engine, and to make this steam engine double-acting. In the engine of Newcomen it was essential that the cold atmosphere should have access to the interior of the cylinder; but Watt devised the plan of using the pressure of steam instead of that of air. In this plan when the piston is at the top of the cylinder, the steam below the piston is now condensed, the communication with the boiler being shut off, while steam from the boiler is admitted above the piston, which thus descends with force; but when at the bottom of the cylinder, the steam above the piston is shut off from the boiler and condensed, while steam from the boiler is

allowed to pass beneath the piston—which is thereby driven upwards with force.

By this arrangement neither cold water nor cold air is admitted into the cylinder, the object being to keep the cylinder always as hot as possible. Moreover, radiation from the heated cylinder into the surrounding air is prevented by a non-conducting envelope or jacket; and frequently in the best engines by a steam-jacket.

358. Expansive working. One other great improvement of Watt requires to be mentioned.

If the communication of the cylinder with the boiler be uninterrupted during the whole time of the stroke of the piston, and if the resistance to the ascent of the piston be uniform, and of course less than the pressure of the steam, the velocity of the piston will gradually increase to the end of the stroke, when its momentum will be suddenly destroyed by striking against the end of the cylinder. Available work will by this means be converted into heat of percussion (an unavailable form), while the engine itself will also suffer in consequence of these blows. Watt checked this by shutting off the communication with the boiler before the piston had yet finished its stroke. The remainder of the stroke would thus be performed under the continually diminishing pressure of the expanding steam, and the piston would reach the end of the cylinder with little or no velocity. Other improvements were introduced into the steam engine by Watt, and also since his day, but these have been chiefly of a mechanical nature and are therefore foreign to the subject of this work.

359. It will be observed that the leading idea in the engine we have described is to produce work as economically as possible, and that this was effected mainly by the improvements of Watt.

The following table will render this evident. It represents

the performance in foot-pounds of different engines for one bushel (somewhat less than 100 lbs.) of coal consumed both before and after the era of Watt.

1769	Atmospheric engine (Smeaton)	5,590,000
1772	" "	9,450,000
1776	Watt "	21,600,000
1778	" (expansive working)	26,600,000
1830	Cornish engines	86,585,000

360. Definition of horse-power. In an engine we have however another point to consider besides the economy with which it works ;—this point is the rate at which it works, or how much work it produces in a given time. The unit of this measure is usually the horse-power. An engine is said to be of one horse power when it will raise 33,000 lbs. one foot high in a minute, this being the average rate of work of the strongest London horses : it is said to be of 10 horse power when it will do ten times this work in one minute, and so on.

361. It will appear as a consequence of the principles deduced in the last chapter that the economy of an engine will be increased by increasing the range of temperature between the source and refrigerator ; but this can scarcely be done to any great extent in the steam engine ; for if the temperature of the water in the boiler is very high the pressure is enormous. Whether on this account any other vapour or gas might not be employed with greater economy is a practical question which has not yet been decided.

362. Locomotive engine. Stephenson. Our object in this sketch has been to furnish the reader with a short account of those improvements in engines which have reference to heat, and before concluding it we cannot do better than describe certain appliances in the locomotive engine. This form of engine is adapted for carrying itself and a load swiftly on iron rails, and was improved very

much by George Stephenson: of late years it has played a very prominent part in the world's history. In this engine the principle of condensation cannot be adopted, as that would lead to a large increase in the weight of the engine in order to hold the necessary water. We have not therefore, as in the ordinary engine, the pressure of steam on one side of the piston and a vacuum on the other, but we have the pressure of steam on one side and that of the air on the other; thus, in the locomotive the steam is generated at high pressure, and instead of being condensed is blown off into the air.

It is necessary that the locomotive boiler should vaporise water as quickly as possible; in order to produce this result metallic tubes conveying the heated air of the furnace pass through the boiler, thus exposing as great an area of the boiler as possible to the action of the heat. Another feature of the locomotive is the blast-pipe, or pipe by means of which the waste steam is made to escape through the chimney, and in so doing to supply a powerful draught to the fire. By this arrangement the fire is urged most when the engine is going most quickly, and when there is therefore most need of rapid combustion.

CHAPTER IV.

Connexion between Heat and other Forms of Energy.

CONNEXION BETWEEN HEAT AND ELECTRICITY IN MOTION.

363. Conversion of electricity in motion into heat. Heat is the ultimate form of energy generally assumed by a current of electricity. Thus when a Leyden jar is dis-

charged a momentary flash of light is seen, and in voltaic currents we know that there is often a great display of heat in those portions of a circuit which most resist the passage of the electrical current.

Until recently it was supposed by some that the electric flash was the direct production of light through the union of the two electricities, and that this flash did not imply the existence of ordinary matter in a heated state; but of late years it has been shewn that the electric flash is probably due to a small portion of some kind of matter intensely heated. Thus when a jar is discharged, or the spark is taken between the terminals of a Ruhmkorff's machine, this spark arises from a small quantity of the matter of the terminal, in a gaseous state and at a very high temperature, combined with a small portion of the air or gas existing between the terminals also intensely heated. Indeed, we can analyse by the prism the light of such a spark, and we find that this light gives the spectrum of the substance composing the terminal in a state of vapour superposed upon the spectrum of the air or other gas existing between the terminals. Great light has been thrown upon the nature and peculiarities of the electric discharge by the introduction of spectrum analysis, and also by the researches of Dr. J. P. Gassiot and others.

The heating effect of the ordinary voltaic current is immediately apparent. Large quantities of wire may be heated to fusion by this current, and the light from charcoal points a little separated is the most brilliant which can be produced by artificial processes. Indeed, the heating effect, and consequently the energy of voltaic electricity far exceeds that of statical electricity, although the potential energy of electrical separation is greater in the latter.

364. Viewing voltaic electricity as an agent capable of measurement continually passing along the wire of a circuit,

the following are the laws which regulate its calorific effect.

Let I denote the *quantity* of electricity which passes in *unit of time* across the section of a wire; or, in other words, let I denote the *intensity* of the current which proceeds along the wire; then the heat produced is proportional to I^2 , and also to the electric resistance R of the wire, that is to say, the heat varies as RI^2 .

Again, R , or the electric resistance, is proportional to the length of the wire, and hence a double length of wire will offer a double resistance; while it is inversely proportional to the area of the cross section of the wire, so that a wire of double sectional area only interposes half the resistance.

We thus see that in such a current, if the wires used be of the same material, the heat developed is directly proportional to the square of the intensity of the current and also to the length of the wire, while it is inversely proportional to the area of the cross section of the wire. For wires of different material but of equal lengths and sectional areas the heating effect is inversely proportional to the electric conductivity.

365. The reason is evident why a current passing along a wire should develop twice as much heat in one which is twice as long, and also why in a wire of half the section it should develop twice as much heat, but it is not quite so apparent why the heating effect should vary as the square of the intensity. This may, however, be very easily explained. Suppose we have two wires of single thickness coiled together, while currents of single intensity are sent simultaneously through each wire—we may if we choose imagine the one current to go through the one wire, and the other current through the other wire. Here then we have a double current going through a double wire, while of

course twice as much heat is developed as when a single current goes through a single wire; but when this double current is made to go through a single wire, twice as much heat will be developed as when it goes through a double wire; that is to say, four times as much heat as when a single current goes through a single wire.

366. It is not within the province of this work to give the theory of the voltaic battery: we will therefore suppose that our readers are already conversant with the arrangement of a simple battery consisting of a number of pairs of copper and zinc. Now it is well known that in such a battery, when the circuit is complete, the intensity of current, or quantity of electricity which passes in an unit of time through every cross section of this circuit, is the same. The intensity being the same for every cross section of the circuit, if we imagine that all the energy of the current is expended in heating the circuit, and if we know the electric conductivity of the various materials of which the circuit is composed, the laws already stated furnish us with the means of finding the distribution of the heat in the different parts of the circuit.

Thus there will be a great heating effect where the resistance is great, and a small heating effect where this is small.

To give a numerical example. Suppose one part of the circuit is composed of a foot of silver wire .05 inch in thickness, while another part is composed of 5 inches of gold wire .01 inch in thickness; it is required to find the relative heating effect of the current in those two parts of the circuit. Calling that produced in the first wire unity, we shall have that in the second wire represented by—

$$1 \times \frac{100}{78} \times \frac{5}{12} \times \frac{(\cdot 05)^2}{(\cdot 01)^2} = 13\cdot 35;$$

where the first multiplier is on account of the difference of

substance (see Art. 168), the second on account of the difference of length, and the third on account of the difference of section.

Knowing thus the relative distribution of the heating effect along the different parts of the circuit, the whole amount of heat produced may be found by bearing in mind the nature of the process which supplies the heat in such a battery. A chemical action goes on between the zinc and the acid in virtue of which electricity is produced: the zinc is burned, and the electrical energy given out is proportional to the quantity of zinc consumed. This electricity is converted into heat by the resistance of the circuit.

Joule has shewn that if the same quantity of zinc be combined with the acid in an ordinary vessel it will give out the same amount of heat as it would if the combination took place by means of the voltaic arrangement, and he has expressed an opinion that heat of combination is in *all* cases first produced as electricity.

The difference between the two processes is not therefore a difference in the amount of heat produced from the same combination—indeed, according to the laws of the conservation of energy there could be no such difference—but it consists in the peculiar distribution of this heat. In the voltaic arrangement, by interposing a resistance in the circuit, heat might be produced many miles from the cells; whereas in the ordinary chemical combination of the zinc with the acid, the heat is of course entirely confined to the vessel in which the combination takes place.

367. Conversion of heat into electricity in motion. Allusion has already been made to the thermo-electric currents produced when a circuit composed of two different metals has the two junctions unequally heated (Art. 163), and it has been stated that in a circuit of bismuth and

antimony the current will go from the bismuth to the antimony across the heated junction, while it goes from the antimony to the bismuth across the cold junction. Suppose now that we have a circuit with both junctions of the same temperature, and that heat is abstracted, let us say, by radiation from the junction *C* (Fig. 78); this junction will therefore lose heat, while, at the same time, an electrical current will be established in the circuit in the direction of the arrow-heads.

Now an electrical current denotes energy; and since there is no access of energy to the system that might become transformed into such a current—but the reverse, since the system is losing heat by radiation—it is clear that some other form of energy must disappear from this system in order to produce this current.

We should naturally look for a disappearance of some of the heat of the system, and it was on this principle that Joule and Lord Kelvin explained the fact (first discovered by Peltier) that a current of electricity passing across a junction in the direction from bismuth to antimony causes cold. For if a current of electricity has such a cooling effect, it ought to be (as it is) when passing from the bismuth to the antimony, and not when passing from the antimony to the bismuth. For let us refer once more to Fig. 78. Since the junction at *C* is colder than that at *H*, and since in consequence a current is passing across *C* in the direction of the arrow-head, if this current has a cooling effect at one of the junctions it ought to be at *H*, for evidently if it cooled *C* (already colder than *H*) and heated *H* (already hotter than *C*) it would result that an electric current, and hence energy capable of performing work, might be associated with the conveyance of heat from a cold



Fig. 78.

junction towards a hot one; that is to say, from a cold substance to a hot one: but this would be in violation of the principle propounded in Art. 334. Such a current therefore will cool *H*, and heat the other parts of the circuit; and if it have no work to do external to the circuit, it will simply act as a means of conveying heat from the hotter to the colder parts of the circuit. But if it accomplish external work, some of the heat of the circuit will disappear as heat in the process of producing this external work.

CONNEXION BETWEEN HEAT AND MOLECULAR POTENTIAL ENERGY.

368. Latent Heat. In most bodies when heated and allowed to expand freely the heat has a double office to perform. A great part of it is no doubt spent in communicating a peculiar motion to the molecules of the body, but some of it is also spent in doing work against the molecular forces of the body; such, for instance, as separating the molecules from each other against the force of attraction which holds them together. More especially may this be the case when a body changes its condition, that is to say, passes from the solid to the liquid or from the liquid to the gaseous state; and we may in many such cases suppose a portion of the heat required to produce this change of state to be spent in doing work against molecular forces.

It will be necessary here to make a remark with regard to the latent heat of vapours, and especially that of steam. Experimentalists have sometimes defined the total heat of saturated steam of any temperature to be the quantity of heat required to convert a unit of weight of water at 0°C into steam of this state.

Now it has been well remarked by Lord Kelvin that the amount of heat necessary to do this depends on the mode

in which the change of state is effected. No doubt the real quantity of heat (kinetic and potential) of a pound of the vapour of water at a certain temperature and pressure is constant, while the heat of a pound of liquid water at 0°C is also constant; but in passing from the one state to the other work is generally done, and the operation may be so varied that in some ways more work may be done than in others. Thus Lord Kelvin remarks that the final quantity of heat required to evaporate a quantity of water at 0°C , and then, keeping it always in the state of saturated vapour, to bring it to the temperature 100°C , cannot be so much as three-fourths of the quantity required first to raise the temperature of the liquid to 100°C and then to evaporate it at that temperature.

Now in a determination of the total heat of aqueous vapour made by Regnault let us see how the experiment was performed. It was conducted virtually in the following manner. To one extremity of the calorimeter a vessel was attached containing water, which was made to boil at a certain constant temperature; and this vapour of water in passing through the calorimeter was given out at the other end as liquid water, let us say, of the same temperature, having been in the meantime robbed of a certain amount of heat, which remained in the calorimeter and was there measured.

Now it is evident, Lord Kelvin remarks, that since no external work is done by this arrangement, and therefore since no heat is converted into work, the whole amount of heat absorbed at the one end in converting the water into vapour at a constant temperature of ebullition is given out at the other in reconverting this vapour into water. Regnault's total heat of steam (Art. 308) is therefore the quantity of heat that would be required first of all to raise the water without evaporation to the proper temperature,

and then to convert it wholly at that temperature into saturated vapour.

369. Gradual change of molecular state. We have spoken of the molecular change that generally accompanies change of temperature of a body; if, however, a body when at a high temperature be suddenly cooled, its particles have not had time to acquire their proper position for the reduced temperature, and they are therefore thrown into a state of constraint. Prince Rupert's drops, formed by dropping melted glass into water, are examples of this class. Now all such bodies tend as far as possible to assume a more natural condition; and on this account a Prince Rupert's drop, if the surface be only slightly scratched, breaks into small pieces. We have seen also that the recently blown bulb of a thermometer gradually contracts. Probably these changes, whether abrupt or gradual, are attended with an evolution of heat, and denote the conversion of potential into kinetic molecular energy.

In other bodies a process of a more complete kind goes on; and there is, in fact, a new arrangement of particles, in virtue of which many of the properties of the body are changed. We see this take place in sulphur, phosphorus, iodide of mercury, &c. In all such cases molecular energy leaves the potential to assume the kinetic form, or it leaves the kinetic form to assume the potential.

CONNEXION BETWEEN HEAT AND THE POTENTIAL ENERGY OF CHEMICAL SEPARATION.

370. Transmutation of the potential energy of chemical separation into heat. In accordance with what has been stated, it is natural to expect that if a definite quantity of carbon or of hydrogen be united to oxygen or burned under given conditions a definite quantity of heat will be produced. Thus a ton of coal or of coke will give out, as

it burns, a definite quantity of heat, neither more nor less. Although this almost seems to be self-evident, yet the difficulties attending a correct estimation of the heat-equivalent of the chemical action which takes place in this and similar combinations are very great. In order to exemplify these difficulties let us suppose that 12 pounds of carbon (a solid) are united to 32 pounds of oxygen (a gas) at a given pressure, the temperature of the constituents being 0°C : the result is the production of 44 pounds of carbonic acid gas. If we wish to find how much heat is due to chemical action we must first of all preserve the heat of combustion so as to measure it by a calorimeter. By this means it may be possible to estimate the whole amount of heat rendered sensible; but something more is still desired if we wish to know the exact heat-equivalent of the chemical combination which has taken place. In order to ascertain this it will be necessary to know—

(1) The total amount of molecular energy (both kinetic and potential) in the carbon *C*.

(2) The total amount of molecular energy in the oxygen *O*.

(3) The total amount of molecular energy in the compound CO_2 .

Now it will be found that (3) is greater than the sum of (1) and (2), the difference denoting the amount of chemical potential energy which has been transmuted into heat. That is to say, the molecular energy of the compound *less* the molecular energy of both constituents united is *equal to* the heat produced by chemical action.

But we have no certain means of estimating directly the whole molecular energy either of the components or of the compound produced, for we cannot deprive any of these bodies of the total amount of its molecular energy and thus measure its amount. We may no doubt by means of measurements of specific and latent heat arrive at conclusions

more or less probable regarding the molecular energy of bodies, but these conclusions cannot be regarded as certainties; and besides, they are founded on experiments of a very difficult nature. It being thus impossible with our present knowledge to estimate with certainty (1), (2), and (3), it is also impossible to estimate with certainty

$$(3) - \{ (1) + (2) \};$$

—an expression which represents the heat-equivalent of chemical action.

371. But though we perhaps cannot in this sense estimate the quantity of energy produced by chemical action, we can cause a certain definite quantity of carbon in a definite molecular state and at a definite temperature to combine with oxygen at a definite temperature and pressure; and when the carbonic acid gas which is the product of combustion has been brought to this same definite temperature and pressure we can find how much heat has been evolved in the process of combustion. Determinations of this nature have been made by many chemists, among whom may be named Crawford, Lavoisier, Dalton, Davy, Dulong, Despretz, and more recently Andrews, Hess, and Favre & Silbermann. As the experiments of Andrews were performed with unusual accuracy we shall now shortly describe his method of observation.

372. *Andrews' experiments.* When the experiments of Andrews were made on gases these were introduced into a vessel of sheet copper, thin, but strong enough to resist the force of the explosion. The copper vessel *a* (Fig. 79), containing the mixed gases, was introduced into another of larger capacity, which was filled with water; the latter vessel was suspended in a cylinder which had a moveable cover at each end, and the whole was finally enclosed in an outer vessel also cylindrical. This outer vessel was capable

of being made to rotate round a horizontal axis by means of the arrangement shewn in the figure. Before commencing the operation the apparatus was made to rotate for some time, in order to bring all its parts into a uniform temperature: this temperature was then measured by a very delicate thermometer. The apparatus was then brought into connexion with a voltaic battery, so arranged that a fine

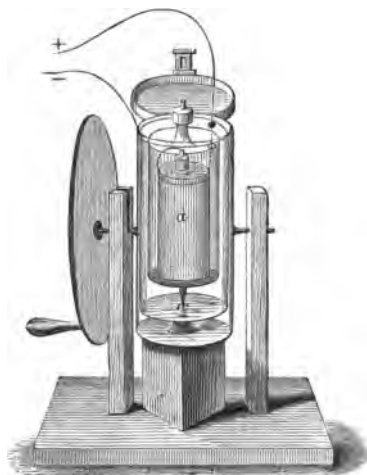


Fig. 79.

platinum wire passing through the gas was by means of the current brought to a red or white heat, and the gas in consequence made to explode. The orifice of the calorimeter was then quickly closed with a cork, the lid shut down, and the whole made to rotate for 35 seconds, in order to distribute the temperature uniformly throughout the apparatus. The thermometer was then again introduced and the increase of temperature observed; by this means, and by knowing the calorific capacity of the apparatus, the amount of heat produced by the explosion might be determined.

A somewhat different form of apparatus was used when solid bodies were burned in oxygen, but the principle of the experiment was the same.

373. The following tables give some of the results obtained by Andrews and Favre & Silbermann:—

Units of heat developed during combustion in Oxygen.

Substance burned.	Pounds of water raised 1°C by the combustion of one pound of each substance.	Compound formed.	Observer.
Hydrogen . . .	34462	H ² O	Favre & Silbermann
" . . .	33808	"	Andrews
Carbon . . .	8080	C O ²	Favre & Silbermann
" . . .	7900	"	Andrews
Sulphur . . .	2220	S O ²	Favre & Silbermann
" . . .	2307	"	Andrews
Phosphorus . . .	5747	P ² O ⁵	"
Zinc . . .	1301	ZnO	"
Iron . . .	1576	Fe ² O ⁴	"
Tin . . .	1233	SnO ²	"
Copper . . .	602	CuO	"
Carbonic oxide	2431	CO ²	"
" . . .	2403		Favre & Silbermann
Marsh gas . . .	13063	"	"
" . . .	13108		Andrews
Olefiant gas . . .	11942		"
" . . .	11858		Favre & Silbermann
Alcohol . . .	6850		Andrews
" . . .	7183		Favre & Silbermann

Units of heat developed during combustion in Chlorine.

Hydrogen . . .	23783	H Cl	Favre & Silbermann
Potassium . . .	2055	K Cl	Andrews
Zinc . . .	1529	Zn Cl ²	"
Iron . . .	1745	Fe ² Cl ³	"
Tin . . .	1079	Sn Cl ⁴	"
Antimony . . .	707	Sb Cl ³	"
Arsenic . . .	994	As Cl ³	"
Copper . . .	961	Cu Cl ²	"

Units of heat developed by the action of Bromine.

Substance burned.	Pounds of water raised 1°C by the combustion of one pound of each substance.	Compound formed.	Observer.
Zinc	1269	Zn Br ²	Andrews
Iron	1277	Fe ³ Br ⁵	„

Units of heat developed by the action of Iodine.

Zinc	819	Zn I ²	Andrews
Iron	463	Fe ³ I ⁵	„

374. Metallic precipitates. Andrews has likewise made a number of experiments on metallic precipitates, and he finds as a result that the quantity of heat developed during the mutual action of two metals, *A* and *B*, when an equivalent of *A* displaces an equivalent of *B* from any of its salts, is the same whatever be the nature of this salt, provided that in all the salts *B* is in the same state of oxidation.

We are thus provided with a means of arranging the metals, beginning with that metal which evolves most heat when used to displace the metal at the other extremity of the series. This furnishes the following list:—

- | | |
|------------|--------------|
| 1. Zinc. | 5. Mercury. |
| 2. Iron. | 6. Silver. |
| 3. Lead. | 7. Platinum. |
| 4. Copper. | |

It is interesting to observe that this is exactly the electro-chemical order of these metals, zinc being the most electro-positive and platinum the most electro-negative.

This prepares us for the following conclusion, also deduced by Andrews.

If there be three metals, *A*, *B*, *C*, such that *A* will displace *B* and *C* from their combinations, while *B* will displace *C*, then the heat developed by substituting *A* for *C* will be equal to that developed by substituting *A* for *B* *plus* that developed by substituting *B* for *C*.

Compare this with the fact that the electro-motive force between *A* and *C* is equal to that between *A* and *B* *plus* that between *B* and *C*, and we are thus led to imagine that the electro-motive forces which are really due to contact of dissimilar bodies are also the very forces which cause heat when chemical combination ensues, potential energy being then converted into kinetic energy by the rushing together of the particles under the attracting forces.

Andrews has also made experiments from which it may be inferred that the quantity of heat given out when different acids combine with an equivalent of the same base is nearly the same, while however the same acid combined with different bases produces different amounts of heat.

375. Nature of flame. This may be the fittest place to say a few words on the nature of flame, for the knowledge of which we are much indebted to Davy.

Let us take a flame of ordinary gas.

This substance consists of carbon united to hydrogen, and is perfectly transparent.

Now when a gas flame is lit we find the lowest part next the burner to have a very feeble luminosity; this part consists of gas more or less heated which has just escaped from the pipe but has not yet united with the oxygen of the air: its temperature is not perhaps very high, but even if it were high, so long as this gas does not change its nature it will give out but little light, the reason being that it absorbs but little (Art. 221). As this gas proceeds upwards it

comes into the presence of the oxygen of the air and unites with it; and the results of this union are certain products the exact composition of which is uncertain, but which both absorb and radiate much more than the lower stratum of heated gas.

376. Heat absorbed when salts dissolve, and the converse of this. During the solution of salts in water heat is generally absorbed, and the temperature of the liquid falls; nevertheless in a few cases there is an evolution of heat when certain anhydrous salts are dissolved.

This is probably due to the preliminary formation of a solid hydrate, a process which is generally accompanied by heat, as for instance, when hydrate of baryta is formed.

On the other hand, heat is evolved during the deposition of a solid from a supersaturated solution.

377. Heat evolved during the solution of gases. We have already noticed (Art. 134) that when a gas is absorbed by water a considerable evolution of heat takes place. We may suppose that this consists not only of the heat due to chemical combination, but also of that due to the latent heat of gaseity which is evolved when the gas passes from the gaseous to the liquid state.

Thus—

1. When water unites with a gas and the product is liquid, we have great heat developed.

2. When water unites with a liquid (such as sulphuric acid) and the product is liquid, we have generally still heat; but

3. When water unites with a solid and the product is liquid, we have often an absorption of heat; while

4. If the product is solid we again have heat.

In the cases now described it would seem to be change of condition as much as chemical action which determines the result as far as heat is concerned.

Heat is also produced when a gas condenses on the surface of a solid.

Pouillet has also shewn that heat is produced in capillary action.

378. Transmutation of heat into the potential energy of chemical separation. When certain bodies are heated they are decomposed; thus, for instance, when carbonate of lime is heated it gives out its carbonic acid, also when slaked lime is heated it gives out its water and is changed into quick lime. Heat is thus transmuted into the potential energy of chemical separation.

Radiant heat (more especially those rays which are called chemical rays) may be directly transformed into the potential energy of chemical separation.

Thus when such rays fall upon chloride of silver we have a chemical change produced which is made use of in photography.

It is believed that this change consists in the decomposition of the salt into its constituents, and that silver is deposited.

Again, when certain rays of the sun fall upon the leaves of plants they become the means of decomposing carbonic acid into oxygen and carbon, the former being set free and the latter assimilated by the plant.

CONNEXION BETWEEN HEAT AND THE POTENTIAL ENERGY OF ELECTRICAL SEPARATION.

379. We have already noticed (Art. 167) that when certain crystals are heated there is a development of statical electricity.

The most prominent laws of the relation between heat and other forms of energy are those which have now been given.

CHAPTER V.

Dissipation of Energy. Sources of Energy. Concluding Problems.

DISSIPATION OF ENERGY.

380. It will have become apparent from the preceding chapters that we can no more create energy than we can create matter, and that all we can do is to make the best possible use of the store of energy at present existing in the universe around us.

Now some forms of energy are of more service to us than others, and we ought therefore to enquire which of the various forms of energy are the most serviceable and which are the least so. Having come to definite ideas on this subject it becomes one of the most interesting, as well as one of the most important, problems to look around us and review the various stores of available energy which have been put at our disposal by the Author of the Universe.

381. We have already seen (Art. 317) that a machine only transmutes energy from one form to another, and that in consequence it is impossible for any machine unless supplied with energy of some kind, either continuously or periodically, to go on doing work ; and that in this sense perpetual motion is impossible.

It will also be seen by Art. 334 that we may modify the usual conception of perpetual motion in a way that will render it not inconsistent with the law of the conservation of energy, although it is nevertheless equally impossible. Indeed, it will appear that the reasoning of Chapter II of this book is founded on the assumption that it is impossible to convert heat into mechanical energy by abstracting it from a substance of lower temperature than the substances

around it, because if this were possible a perpetual motion would be possible also ; nevertheless, such a perpetual motion is not inconsistent with the principle of the conservation of energy. Now when we come to examine more closely into the results of this chapter we see that the impossibility of this form of perpetual motion is intimately connected with the fact that heat tends to diffuse itself.

382. The following example will make this plain. Suppose a machine to perform work in a room that neither conducts nor radiates heat to other bodies ; that is, in fact, isolated as far as regards the reception or communication of energy with the rest of the universe.

Suppose, further, that the source of this machine is supplied with heat, and that in consequence of this the machine does work. Next suppose that this work, by means of friction or otherwise, is immediately reconverted into heat, and then carried again to the source of the engine.

Will not such an engine, it may be asked, go on working for ever? There is nothing in the law of the conservation of energy that forbids this result, for the energy of the chamber is supposed to be constant, while a constant proportion of this energy is supposed to exist always in the shape of mechanical work. The possibility of this arrangement is connected therefore with the possibility of *wholly* reconvertng the heat produced by the mechanical motion into motion, which is again to be converted into heat, and from heat into motion, and so on for ever.

To assume the most favourable circumstances, let us suppose that there is absolute zero of temperature in the chamber, except at the source of the engine ; then, assuming the truth of the results of Chapter II, we may conclude that if a quantity Q of heat be taken from the source it will be wholly converted into work. Suppose, again, that the work is reconverted into heat in a box similar to the chamber itself—

that is to say, neither conducting nor radiating heat—and that this heated box is taken back to the source, reconverted there entirely into work, and so on.

No doubt this arrangement would be, in its literal sense, a perpetual motion—but not in the technical sense, as no external work is produced. When, however, we come to analyse the conditions we have imposed upon the materials employed, we find that they are such as never occur in nature; there is, in fact, no body that neither conducts nor radiates heat, and it is this tendency to diffusion in heat that prevents the arrangement from being possible. Owing to this tendency it is impossible either to procure a chamber which neither conducts nor radiates, or to produce a perfect zero of temperature. Now this latter is quite essential to the perpetuity of our supposed arrangement; for, without such a zero, while all the work is converted into heat only a portion of the heat is reconverted into work.

The work will thus at every cycle bear a continually diminishing proportion to the heat, and the final result will be a uniform distribution of this latter form of energy.

383. This example, in which the results of Chapter II are taken for granted, forms of course no new proof of the impossibility of this kind of perpetual motion, because the assumption of this impossibility is the foundation of the argument of that chapter. But the example serves to shew that this impossibility is intimately connected with the diffusive nature of heat.

384. All this has been clearly shewn by Lord Kelvin, to whom the principle of the dissipation of energy is due.

He has shewn that when mechanical energy is transmuted into heat by friction or otherwise there is always a degradation in the form of the energy; and inasmuch as this heat cannot be entirely converted back again into work, from its diffusive nature, the final result of continually converting

mechanical motion into heat will be that the amount of mechanical motion obtainable from the system will be always growing less, until ultimately all the energy has taken the unavailable form of equally diffused heat.

That this form of energy is unavailable will be acknowledged at once by recalling to mind the statement that to get work from heat you must have bodies of different temperatures.

385. Suppose now that we have a ton of water at 100°C , while all the other substances around us are at 0° , we have in this ton of water an instrument capable of affording us a certain amount of mechanical work by using it as the source of a perfect engine. There is a certain amount of *available work* in this ton of water, and do what we may we cannot get it to give more, although it may very probably, if improperly used, give less work. It would appear that by no artifice can we increase this amount, any more than we can increase the available work of a head of water of given contents and height of fall.

It might perhaps be thought that this would be possible if we could convert the heat of this water into the potential energy of chemical decomposition; could we not use it to decompose a certain amount of some compound substance whose components have a great attraction for one another, so that by the reunion of these components a very high temperature might be produced, the heat of 100°C being thus converted into heat of a higher temperature which would be more *available*? or might not the radiant heat from the water be used to produce some kind of chemical decomposition, and thus the same result be obtained?

It is believed that any such result is, to say the least, unlikely: in fact, it has been remarked by Lord Kelvin that an intimation to this effect seems to be given by nature, for we have no reason to think that either absorbed

or radiant heat of low temperature is easily capable of producing powerful chemical changes of this nature.

There is no reason to think that this stratagem of bringing in chemical decomposition will increase the amount of available work to be obtained from one ton of hot water, and in our ignorance of the ultimate constitution of matter it would appear that the principle of the degradation and dissipation of energy, just as that of the conservation of energy, should be recognized as a principle having very strong claims to recognition and as increasing these claims every day by the new facts which its employment as an instrument of research is constantly bringing to light.

At the same time it is but just to state that the principle of the conservation of energy is at present more fully established than that of the dissipation of energy.

386. Regarding, therefore, uniformly diffused heat as a form of energy utterly unavailable, and regarding mechanical energy as ultimately tending to assume this degraded form when it is reduced by friction, percussion, or otherwise, the question arises, Are there any influences at work tending thus to degrade the motions of the universe? Now we know very well that all motions on the surface of our earth ultimately tend to be dissipated and converted into equally diffused heat; we know also that the heat of the sun and stars tend to assume this degraded form; but does the same reasoning apply to celestial motions? This leads us to ask if there is a material medium pervading space; and also if we have any reason to believe its properties to be such that something analogous to friction takes place; if so, the result would appear to be the conversion, at a rate more or less rapid, of the mechanical energy of the universe into the degraded form of diffused heat.

387. Medium pervading space. We have several reasons for assuming the existence of such a medium.

1. The various phenomena of light are best explained on the supposition that this agent consists of undulations in a medium pervading space.

2. The continual shortening of the path of Encke's comet may perhaps lead us to the same conclusion ; that is to say, to a belief in the existence of a material medium pervading space.

3. We may here allude to certain experiments performed by the author of this work and by Professor Tait, in which a disk of metal or of ebonite was made to rotate with great rapidity in *vacuo*. In consequence of this rotation the substance of the disk was found to be perceptibly heated, and the heating effect appeared, in part at least, to be independent both of the chemical nature and of the pressure of the residual air which remained in the vacuum chamber.

4. The theory of energy affords us a proof in favour of the existence of a medium capable of ultimately stopping all differential motions.

For let *AB* (Fig. 80) represent an enclosure of constant

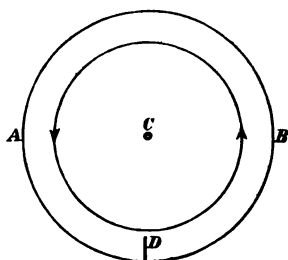


Fig. 80.

temperature, say 0°C , and *C* a black body in this enclosure, of the same temperature as the enclosure itself, and in rapid motion about an axis in the direction indicated by the arrow heads. Let *D* represent a diaphragm which extends from the walls of the enclosure nearly to the revolving body.

Further, let us imagine that there is no gas and nothing but the ethereal medium in this enclosure, and that the experiment is carried on in some space devoid of the gravitating influence of a large planet like the earth ; in fine, let us suppose the interior revolving body to remain suspended

in the midst of the enclosure. Let us now consider that portion of the walls of the enclosure immediately to the left of the diaphragm, and let us suppose that it consists of a stratum of colourless glass. At the moment of commencing the experiment we have supposed everything (enclosure, body, and diaphragm) to be of an uniform temperature 0°C ; now it is easy to show that this equality will not continue. For (Art. 239) we have seen that the nature of the heat radiated by the revolving body *C* which falls upon the glass to the left of the diaphragm will be altered in wave length by the rapidity of revolution of this body, for owing to the interposition of the diaphragm all the particles of the revolving body that radiate towards this glass are at the same time rapidly approaching it. As far, therefore, as this glass is concerned the average wave length of the radiation from *C* will be less than had the body been at rest, and we may, as far as our argument is concerned, suppose the rotation to be so violent that the low temperature heat radiated by the revolving body towards the glass is so much shortened in wave length as to be changed into a kind of heat, which is not absorbed by the glass but passes through it. On the other hand, the heat radiated by the glass will (Art. 195) depend only on the temperature of the glass, and will not be influenced by the revolving body. The glass will thus radiate more than it absorbs, and its temperature will in consequence fall. The equilibrium of temperature with which we started will thus be speedily destroyed, and the various parts of the enclosure will be of different temperatures. But in this case it is possible by appropriate machinery to convert part of this heat of various temperatures into work, for as soon as we have two temperatures a heat engine becomes possible. Now can we suppose an indefinitely large amount of additional mechanical work to be produced from a series of bodies, all of which are initially at the same

temperature? We think not—the theory of energy forbids the supposition; yet this is what will take place under these easily conceivable circumstances, *unless we suppose that the central body has meanwhile lost a portion of its energy of rotation sufficient, at any rate, to make up for the additional work which has been produced.* In other words, we are driven to suppose that a body moving through ether, in such a manner as to change its position with regard to neighbouring bodies, will ultimately have its differential motion stopped by means of the medium.

If, therefore, there be a resisting medium of this nature pervading space, the visible motions of the universe must gradually be lessened in consequence, unless indeed we assume the existence of some unknown completely restorative process; but such a process is inconsistent both with the principle of the degradation of energy and also with the shortening of the path of Encke's comet, whatever mass this may have.

There can, in fine, be little doubt that, if we suppose the principle of the degradation of energy to hold throughout the universe, it implies an element of decay in the present order of things, and the final transmutation of all available energy into uniformly diffused heat, unless we suppose the constitution of the universe to be such that this process of degradation will last an infinite time.

For a clear statement of this subject we may refer our readers to a treatise on 'Thermodynamics' by Professor Tait.

SOURCES OF ENERGY.

388. Let us now consider shortly the various supplies of energy of different kinds with which we are furnished, and also the *ultimate sources* of these supplies.

Of potential forms of energy we have—

1. The potential energy of fuel.
2. The potential energy of food.
3. The potential energy of a head of water.
4. The potential energy derived from the tides.
5. The potential energy of the chemical separation implied in native sulphur, native iron, &c.

Then with regard to kinetic forms of energy, we have—

6. The kinetic energy of air in motion.
7. The kinetic energy of water in motion.
8. We may add to this catalogue the direct rays of the sun which are available for certain purposes ; and also
9. The energy that may be derived from the unequal temperature of different parts of the earth.

389. Fuel and food. The potential energies of fuel and food are of essential importance to our existence.

By fuel we mean certain substances which are capable of combining with oxygen, and of supplying us as they so combine with a large amount of heat of high temperature.

Coal is the most important of such substances ; and we can employ it either to warm ourselves and our habitations by means of the heat which it produces, or as an agent for generating mechanical effect in our various heat engines.

When we come to consider from what original source of energy the chemical separation of fuel is derived, we see that it is due to the sun's rays. These rays acting upon the leaves of plants produce those decompositions which form fuel. The energy of the sun's rays have in fact been transmuted into the potential energy of chemical separation.

This fact seems to have been recognized at a comparatively early period by Herschel and the elder Stephenson ; and a curious tale is current about the latter, who, though well aware that it was the sun that drove his engines, could

not give a very clear explanation of the subject ; nevertheless the statement is undoubtedly true.

It is indeed true that the rays of the sun, acting upon the leaves of plants in those remote ages when coal beds were being formed, have laid up for man a stock of energy of inestimable value.

Food has the same origin as fuel, with the exception that vegetable food is being produced by the sun year by year, while the greater portion of our fuel, as we have just seen, has been produced ages ago. And here we may remark a very prominent distinction between vegetables and animals as regards energy. Vegetables serve to transmute the energy of the sun's rays into fuel and food. Animals, again, consume this food and transmute it partly into useful work, but partly into the degraded form of diffused heat.

Joule, Carpenter, and Mayer seem to have been aware of the restrictions under which living beings are placed by the laws of energy, and to have seen that the power of an animal, as far as energy is concerned, is not *creative* but only *directive*.

A clear view of this subject was probably also held by Rumford. Finally, Helmholtz has treated this question, as well as the whole subject of energy, in a very able manner. An animal is in fact an engine, and just as an engine must be fed with fuel, so an animal must be fed with food.

390. Head of water. We thus see that the sun's rays are the ultimate source of fuel and food, and we have no difficulty in recognizing the same cause as the origin of the energy derived from a head of water. It is the sun that produces rain by promoting evaporation ; his energy is consumed in lifting the water of the earth to a higher level, and we are thus enabled to make use of the potential energy of this elevated water.

391. Tidal energy. The energy capable of being de-

rived from the ebb and flow of the tides has however a different source.

This was recognized by Kant; Mayer also and J. Thomson (the former of whom was the first to give his conclusions a general publicity) shewed that, the ebb and flow of the tides being due to the earth's revolving on her axis while acted on by the moon, the energy of the tides is really taken from the energy of the earth's revolution, part of which is thus ultimately dissipated in the heat of friction caused by the tides: and the astronomical phenomenon known as the secular acceleration of the moon's mean motion is now supposed to be partly caused by a very slow lengthening out of the sidereal day caused by loss of the earth's motion of rotation from this effect of the tides.

It is clear that this action would be arrested when the rotation of the earth was so much diminished that she always turned the same face to the moon, for then there would be no tidal ebb and flow and consequently no friction; and Professor Frankland in a lecture at the Royal Institution, as well as Thomson (Lord Kelvin) and Tait in their treatise on Natural Philosophy, have independently remarked that the much more powerful influence of the earth upon the fluid matter of the moon during the course of ages has probably stopped the rotation of our satellite so far as to cause her always to present the same face to the earth. We thus see that any work we derive from tidal action is abstracted from the motion of rotation of the earth.

392. Native sulphur, &c. The potential energy of the chemical separation implied in native sulphur, iron, &c., is, it may be, the primeval form of energy, but the amount of this energy so far as we know is very small, though the interior of the earth may be wholly made up of matter in an uncombined form. As a source of energy it is at present of no importance.

393. Air and water in motion. The kinetic energy of air in motion, and the kinetic energy of water in motion, are both chiefly due to the sun.

394. Unequal temperature of the globe. Little energy is likely to be derived from the unequal temperature of different parts of the earth, for such differences of temperature are comparatively small, and consequently only a very small proportion of the whole amount of heat transferred from the higher to the lower temperature can be turned to practical account.

395. Now if we group together the really serviceable members of the list of sources of energy, we find that they consist of the potential energies of fuel, of food, of a head of water, and of tidal ebb and flow, together with the kinetic energies of air in motion and of water in motion. All these either are or may be of immense service to man.

396. Coal. Of the different forms of fuel coal is one of the most important, and the exhaustion at no very distant date of this source of energy has been of late very much and very properly discussed.

There appears to be little doubt that the progress of civilisation forces us to draw each year more and more largely upon our stores of coal, and there is no doubt that when once the deposits near the surface have been exhausted those at a greater depth will have a much smaller real value.

For the time, the capital and the labour spent in bringing a ton of coal from a great depth to the surface ultimately resolve themselves into so much available energy spent in accomplishing this: now if a considerable portion of the available energy of a ton of coal is spent in bringing it to the surface, the ultimate value to us of this ton of coal is greatly impaired.

If the question be asked, What shall we do when coal fails? the only reply is, Make as much use as possible of water and tidal power and of the energy of air and water in motion, and plant trees.

It is difficult to think of anything else, or to deny the fact that, as far as we are able to judge, the exhaustion of our coal beds will be a very serious loss of power.

397. The sun. It thus appears that if we except tidal power, the sun's rays are the ultimate source of the available forms of energy with which we are surrounded.

We cannot, therefore, do better than direct attention to this most wonderful source of energy.

398. Actinometric observations. In the first place, let us briefly allude to the attempts that have been made to estimate the amount of the sun's radiant energy, and then let us attempt to speculate on its most probable source.

Instruments for measuring the intensity of the sun's radiant heat have been devised by Herschel and Pouillet. The instrument of the latter he called a pyrheliometer, and it is constructed on the following principle:—

A shallow cylindrical box (Fig. 81) made of iron or steel is filled with mercury. Into this box, and therefore into this mercury, a thermometer is introduced, the stem of which is suitably protected.

At the other extremity of the instrument we have a disc of the same diameter as the box.

Now if the instrument be pointed in such a manner that the shadow of the box, thrown by the sun, coincides with the disc, then we may be sure that the sun's rays impinge perpendicularly on the surface of the box.

The experiment consists of three parts—

First, let the instrument, sheltered from the sun, be permitted to radiate its heat into the clear sky for five minutes. Let the heat lost be r .

Next, let it be turned to the sun for five minutes. Let the heat gained be R .

Finally, let it (at its increased temperature) be allowed to radiate into the clear sky as before for five minutes, and let the heat lost be r' .

Now, since r denotes the radiation into clear sky before

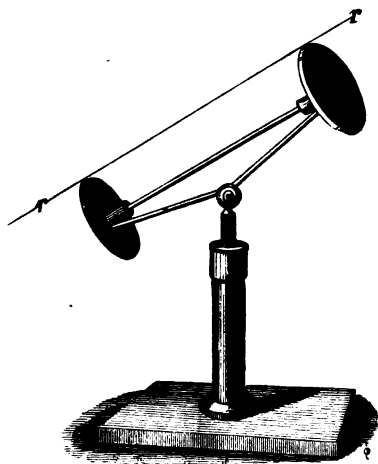


Fig. 81.

heating, and r' the same after heating, the radiation into the clear sky during the heating will be very nearly a mean between the two, or $\frac{r+r'}{2}$; but it is evident that this radiation takes place even when the instrument is receiving the sun's rays, and tends therefore to diminish the heating effect produced by these rays.

Hence, therefore, the whole heating effect will be—

$$R + \frac{r+r'}{2}.$$

It having occurred to the writer that it would be desirable

to construct an actinometer in which the causes of variability are reduced to a minimum, he attempted to do so in the following manner:—

The instrument consists of a large mercurial thermometer with its bulb in the middle of a cubical chamber of brass,

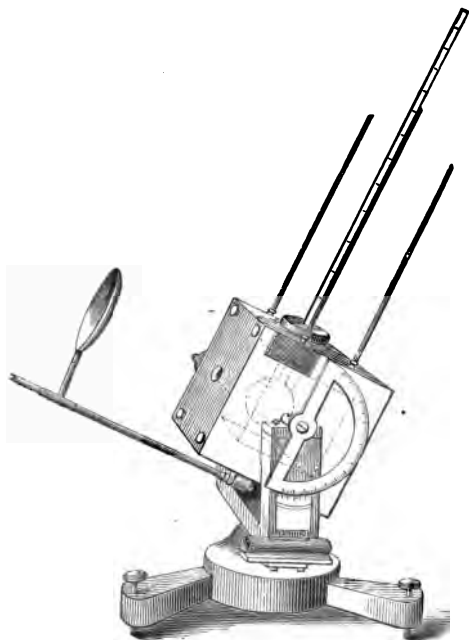


Fig. 82.

this chamber being so massive that its temperature will remain sensibly constant for some time (the bulb is denoted by dotted lines in Fig. 82)¹. The chamber with its thermometer has a motion in azimuth round a vertical axis, and also a motion in altitude round a horizontal axis.

¹ For this figure I am indebted to the kindness of the Science and Art Department, South Kensington.

A lens of suitable aperture (which may be varied by diaphragms), and also of appropriate focal length, is attached by means of a rod to the cubical chamber, so as to move with it. Thus the whole instrument may be easily moved into such a position that the lens, as well as the upper side of the chamber (which is parallel to the plane of the lens), may face the sun, and an image of the sun be thrown through a hole in the side of the chamber upon the thermometer bulb. This hole is covered or uncovered by means of a slide. In the accompanying sketch the beam of rays falling through the uncovered hole upon the bulb is represented by dotted lines. Of course this hole is only uncovered when an observation is being made. The stem of the thermometer protrudes from the chamber as in the figure. A screw, somewhat larger in diameter than the bulb of the thermometer, is made use of in order to attach the thermometer to its enclosure; and a smaller screw, pressing home upon india-rubber washers, enables the thermometer to be properly adjusted, and kept tight when in adjustment.

The stem is about 18 inches long, and about five degrees go to the inch, thus the scale is very open. The stem is protected from the risk of accident by an appropriate shield. By means of a stem of this length it is probable that sufficient range will be secured to provide for observations all the year round at most stations. It may, however, be that in certain localities the summer temperature is very high and the winter temperature very low. In such a case it will be desirable to have two thermometers, one for winter and one for summer use; the scale of the one overlapping that of the other to some extent.

The massive brass chamber is lined with a covering of felt, and this again is surrounded by polished brass plates. By this means the heat of the sun will be to a great extent reflected off, and that which is absorbed having to pass

through the felt, which is a bad conductor, will only be able to raise with extreme slowness the temperature of the massive brass chamber within.

In such an instrument, therefore, r and r' will be very small, and we may be quite certain that $R + \frac{r+r'}{2}$ will accurately represent the heating effect of the sun.

The sketch now given exhibits an improvement introduced by General Strachey, consisting of a graduated arc by which the sun's altitude during an observation can be read off with a sufficient amount of accuracy.

Observations have been made by Herschel and Forbes with Herschel's actinometer, and by Pouillet with his own instrument.

From all these observations it is probable that, taking the earth's hemisphere which is illuminated, one half of the radiant heat of the sun may perhaps reach the ground, the other half being absorbed by the atmosphere. Taking this into account, and imagining for a moment that the earth has no atmosphere, it is calculated that the amount of solar heat received by the earth in one year would liquefy a layer of ice, 100 feet thick, covering the whole surface of the earth.

If we bear in mind that the solar heat which reaches the earth in any time is only $\frac{1}{2,300,000,000}$ of the heat which leaves the sun, we may obtain some idea of the enormous heating power of the radiation from our luminary.

399. Origin of the sun's heat. The most plausible theory of the origin of the sun's heat is that which supposes that the primeval potential energy of gravitation has been converted into heat for the sun's particles.

The rudiments of such an idea seem to have occurred to Mayer and to Waterston; but Helmholtz and Lord Kelvin

have worked it out in such a manner as almost to prove that there is no other known power capable of producing such a stupendous result.

According to this theory we may imagine the particles of matter when originally produced to have been at a distance from each other, but endowed with the power of gravitation, forming in fact a chaotic mass.

As these particles rushed together heat would be generated, just as when a stone is hurled from the top of a precipice, heat is the ultimate form into which the potential energy of the stone is converted.

It is probable that this cause, by storing up an amount of heat in the sun, is sufficient to account for his wonderful outpouring of light and heat during a long series of ages.

We are thus led to regard our own sun and other suns, in fact the whole visible universe, as an existence which had its beginning in a chaotic state of particles endowed with gravitating force, and which will come to a termination, at least as far as useful energy is concerned, when the heat into which the other forms of energy are being gradually converted shall have been equally diffused throughout the whole mass.

It ought however to be borne in mind that our knowledge of the laws of matter is in reality very limited.

CONCLUDING PROBLEMS.

400. Before concluding this treatise let us bring before our readers a few problems connected with the dynamical theory of heat.

401. **Effect of pressure in lowering the freezing-point of water.** In a previous part of this work (Art. '92) it was mentioned that the application of pressure lowers the freezing-point of water, and that Professor J. Thomson was

the first to suggest and prove that this would be the case, while the experiment was first made by Lord Kelvin.

The following explanation of this effect of pressure upon ice is that given by Professor J. Thomson.

Suppose we have a quantity of mercury constantly kept at 0°C as our source of heat, and also a quantity constantly kept at $-\tau^{\circ}\text{C}$ (τ being small) as our refrigerator. Suppose also that we have a cylinder, of which the sectional area is one square mètre, and that this cylinder contains one cubic mètre of water at 0°C ; the water will thus be one mètre high in the cylinder. Suppose now that a pressure equal, let us say, to one atmosphere of 760 millimètres of mercury is caused by placing a mass of 10333 kilogrammes (Art. 332) above the surface of the water in this cylinder; imagine further, for the sake of simplicity, that the material of the cylinder is inexpandible, and its specific heat, as well as that of the mass, is exceedingly small, so that on heating or cooling it is merely the specific heat of the water that we have to consider.

Let this arrangement be now used as a heat engine, and let us first suppose that the cylinder is placed in the mercury at 0°C . Let it next be taken out of this mercury (the contained water being unfrozen) and plunged into the mercury of the refrigerator at $-\tau^{\circ}$; the water will in course of time be frozen, and while freezing it will expand and finally occupy 1.089 cubic mètres; hence the weight of 10333 kilogrammes will have been raised nearly .089 mètre. Suppose now that the cylinder is again transferred to the mercury at 0°C , the ice in the cylinder will in course of time become water and occupy once more its old level one mètre high in the cylinder. There will thus be a void space of .089 of a mètre in height, through which the mass may be made to fall, thus doing useful work, when the process of melting is finished. We have thus obtained work

$= 10333 \times .089 = 919.64$ kilogrammètres for every cycle of operations. Now during each cycle it will be seen that an amount of heat equal to the latent heat of fusion of a cubic mètre of water is conveyed from the higher to the lower temperature. We thus know the quantity of heat conveyed from the source to the refrigerator as well as the quantity of work done. But we also know that this arrangement (Art. 334) cannot possibly give us more work under the circumstances than a perfect engine: in fact we shall see at last that the arrangement is a perfect engine; hence it follows that there must be a certain difference in temperature between the source and the refrigerator. This difference of temperature is easily found.

The latent heat of fusion of a kilogramme of ice (Art. 305) is 79.25 heat units, and hence that of a cubic mètre of water, or 1000 kilogrammes, will be 79,250 heat units. Multiplying by the mechanical equivalent of a heat unit, or 426 (Art. 331 a), we find the total amount of energy transferred from the higher to the lower source during a complete cycle to be 33,760,500. But we have seen that during this process mechanical energy = 919.64 is obtained. Now we know (Art. 346) that in a perfect engine the energy utilised bears to the whole energy of the heat carried from the source to the refrigerator the same proportion as the temperature-difference between the source and refrigerator does to the absolute temperature of the source.

Hence, since 273° (Art. 343) is the absolute temperature corresponding to 0°C , we have the following proportion—

$$33,760,500 : 919.64 :: 273 : \tau ; \quad \therefore \tau = .0074^{\circ}\text{C}.$$

Now if the pressure under which the water expands into ice be doubled or become two atmospheres, twice as much work will be done by this arrangement and twice the above temperature-difference between the source and the refrigerator will be absolutely necessary; in fact, for each

atmosphere of pressure it is necessary to have a difference of $.0074^{\circ}\text{C}$. This is only another way of stating that for each atmosphere of pressure the freezing-point of ice will be reduced by $.0074^{\circ}\text{C}$. For a pressure of 16.8 atmospheres this would give $.124^{\circ}\text{C}$, a result which agrees very closely with the temperature-reduction in the freezing-point of water found experimentally by Lord Kelvin for this same pressure.

A little consideration will shew that the arrangement we have here sketched for producing work by means of the freezing of water is in reality a perfect engine.

402. Temperature. If we refer to Art. 67 of this work it will be found that the whole subject of temperature has been left in a somewhat unsatisfactory condition.

When we analyse our conception of temperature we find it to be this—

If two bodies, such as water and mercury, be brought together, and if neither parts with any of its heat to the other, then each of these two bodies is of the same temperature. If the water parts with some of its heat to the mercury, the water is said to be of a higher temperature than the mercury. On the other hand, if the water receives heat from the mercury, then the water is said to be of a lower temperature than the mercury.

It will be seen that this definition of temperature is very similar to our definition of hardness. If when two bodies are brought together *A* scratches *B*, then *A* is said to be harder than *B*; but if *B* scratches *A*, then *B* is said to be harder than *A*.

Now by means of this definition of temperature or of hardness we are quite able to construct a scale of temperature or of hardness in which we are certain that a body having a definite place in the scale shall be less hot or less hard than that above it, but more hot or more hard than

that below it. We may be able to do all this without at the same time being able to estimate either temperature or hardness quantitatively, and without being able to say that the temperature or hardness of a certain body is precisely half-way between the temperature or hardness of two other bodies.

It may, however, be asked, Do we not then measure temperature by means of thermometers? To this it may be replied, We do not measure temperature: by liquid thermometers we measure expansion; by the air thermometer either expansion or pressure.

We insert a liquid into a glass envelope, and finding that it increases in bulk a certain amount between 0° and 100°C , we assume that half the increase of bulk will denote a temperature half-way between these two points.

We then try different liquids and make them into standard thermometers, but finding they disagree slightly among themselves, we pronounce them unsatisfactory.

We then try the so-called permanent gases of sufficient tenuity, and finding that while they all slightly disagree with liquid thermometers they quite agree amongst themselves, we consider them satisfactory.

403. Before proceeding further it is well to observe that some very eminent scientific men have supposed that our subdivision of a certain temperature-difference is in the nature of things arbitrary, and that all we can do is to subdivide this difference between two temperatures by means of a certain instrument which may be easily reproduced and always remains comparable with itself. Thus, for instance, if we can blow bulbs of invariably the same kind of glass, these when filled with pure mercury will form thermometers always comparable with themselves, and will thus afford us a thermometric scale. But if we fill these bulbs with water instead of with mercury, we produce another set of thermo-

meters also comparable among themselves, but not quite-comparable with the mercurial thermometers.

It may be asked, Which of the two are we to adopt?

It may also be asked, Even if our mode of subdividing a temperature-difference be essentially arbitrary, may not some one conventional mode be better than others?

Now if we take the so-called permanent gases of sufficient tenuity we know that by their means we can produce thermometers comparable with one another, even although we vary the nature of the gas. In such thermometers we measure either the *volume* or the *pressure* of the gas. But if instead of measuring the pressure or the volume we measure the *quantity of heat that enters into our gas* on the convention that equal increments of heat denote equal increments of temperature, we here obtain a scale precisely the same as that obtained by measuring the volume or the pressure of the gas, since the specific heat of the permanent gases remains constant.

Yet, again, Lord Kelvin has shewn that if we measure a temperature-difference by the proportion of a certain quantity of heat Q , passing from the higher to the lower temperature, that is capable of being converted into mechanical effect (Art. 346), we obtain a temperature-scale holding for all bodies, whether liquid, solid, or gaseous, and also precisely the same as that of the air-thermometer.

Finally, in the case of gases of which the molecular constitution is comparatively simple we have some grounds for supposing that we have at length succeeded to some extent in ascertaining what kind of motion constitutes heat. According to this theory, which has been greatly developed by Clausius and Clerk-Maxwell, the particles of gases are supposed to be in continual motion backwards and forwards on account of the heat they contain; in fact, they knock against the sides of the containing vessel, and it is this

knocking that constitutes the pressure : also on this account they tend to intermingle with one another even against the influence of specific gravity, and it is this which constitutes gaseous diffusion. We thus see why the pressure of a gas increases when it is heated.

404. Molecular theory of gases. Here it may be well to consider some of the chief results of the theory to which allusion has just been made. For further information the reader is referred to Professor Clerk-Maxwell's book on the Theory of Heat.

The dynamical theory of gases was first suggested by Daniel Bernouilli, and was afterwards extended by Lesage, Prévost, Herapath, Joule, and Krönig, but we are indebted to Clausius and especially to Clerk-Maxwell and Boltzmann for the great development which has recently taken place. Still more recently Crookes has made important experimental investigations, while Professor O. Reynolds has added much to the theory of the subject.

405. It is assumed in this theory that all bodies consist of molecules with spaces between them of a greater or less extent. The structure of matter is thus a grained one, and we have even some reason to believe that we have been able to form a rough estimate of the size of these grains. The molecule is the smallest part of a substance that is capable of possessing all the chemical properties of the substance ; thus a molecule of chloride of sodium is still chloride of sodium, but if we suppose it to be further divided it will split up into two distinct things, namely, chlorine on the one hand, and sodium on the other. A single molecule may, and generally does, consist of various portions of matter, these being bound together by chemical forces, and bound together in a very strong way. In solids, besides the forces which bind together the various constituents of molecules, there are also strong forces, binding together the

various whole molecules, and these forces are comparable in intensity, it may be, to the forces which bind together the various parts of a single molecule—from which it follows that in solids there are definite and in general very narrow limits to the excursions of the molecules.

In liquids, however, there are fewer restrictions to such excursions, while in gases a molecule has very great freedom of motion. Therefore in a heated gas we may imagine a molecule in virtue of the motion whose energy we call heat to move a considerable distance before it encounters another molecule—in other words, to have a comparatively great free path. For the greater part of its excursion such a molecule may be supposed to move in a straight line, but ultimately it encounters either another molecule or the side of the containing vessel, and the result is a change in its motion.

406. The number of such molecules being very great it is impossible to keep a record of the varying parts of the path of any one individual, so that, in studying these encounters and their results, we must resort to the statistical method of inquiry by which we may often obtain very great knowledge of the laws that regulate communities while we are yet in profound ignorance of individual experiences.

407. Now a little consideration will render it evident that in this molecular warfare the tendency is not to a uniform distribution of velocity among the particles, and that if we imagine such a state to exist for one moment the next moment it would be destroyed. For one particle may have its velocity entirely stopped by an encounter, while another moving previously with a very great velocity may nevertheless have its velocity increased by an encounter at right-angles.

408. Nevertheless there is a tendency towards a certain average velocity among the particles, because, if we are

dealing with gas of constant temperature it is clear that the whole amount of molecular energy remains constant.

We cannot therefore imagine that a considerable proportion of the particles can have at any moment a velocity differing very greatly from the average, as for instance a very small or very great velocity. In fine there must be few particles that at any moment possess a velocity greatly differing from the average compared with the number that possess a velocity nearly coinciding with the average.

409. Now inasmuch as we are pursuing the statistical method of inquiry, let us distribute the molecules into groups, according to the velocity with which they are moving—each group comprehending velocities between certain limits.

Doubtless if we take a very great (almost infinite) number of groups and regard each for an exceedingly small interval of time, it may chance that the number of molecules belonging to the group may vary from one moment to another. But if we regard only a finite, though large number of groups, and study each for considerable successive intervals of time, such as minutes for instance, there is then no reason why the number belonging to such a group should be greater during one minute than another. The law however of the distribution of the velocities amongst the various groups of molecules is given by means of a mathematical investigation which we cannot here reproduce.

410. Again, since it is the energy or vis viva of the whole system that remains constant, and since energy is proportional to the square of velocity, in our investigations it is best to consider the mean of the squares of all the velocities—this is called the *Mean Square of the velocity*, and its square root is called the *Velocity of Mean Square*.

411. One of the most important questions is to determine what will happen when in the same vessel we have two

different kinds of gas, the molecules of which have different masses.

Now it may be shewn by means of the same mathematical investigation which gives us the law of distribution of velocities where we have only one kind of molecule, that when we have two kinds the average kinetic energy of agitation of the one set will be equal to that of the other. In other words, if we have the same number of molecules of both kinds thus existing at the same temperature, then the one set will have the same kinetic energy of agitation as the other. We cannot however reproduce this investigation here.

412. The dynamical theory gives us an easy explanation of the pressure of a gas.

Let us begin by imagining a plane surface of unit area to form part of the enclosure of a vessel containing gas. Again, let us take those molecules of which the velocity-component differs very little from u in a direction perpendicular to, and moving towards this surface, and let us denominate by the letters v and w all velocities in two other directions parallel to the plane and perpendicular to each other. Let us suppose there are N such molecules in every unit of volume and that the mass of each is M . Then evidently a number of such molecules represented by Nu will strike this area in unit of time, and the resolved portion of the momentum of each in a direction perpendicular to the area will be Mu . Hence the momentum due to such molecules reaching the area and striking against it will in unit of time be MNu^2 .

413. Now if we perform the same operation for every other group of molecules moving towards the plane surface, we shall obtain a sum which we may represent by $M\Sigma(Nu^2)$ as denoting the whole momentum that impinges perpendicularly against the plane in unit of time.

Again, since the elasticity is supposed to be perfect in

the molecular impacts we are now considering, we may imagine the impinging particles to rebound from the enclosure and to form in consequence of this rebound a current of particles coming from the enclosure, the vis viva of the return current being the same as that of the advancing current, but the resolved portion of the velocity in a line perpendicular to the enclosure being reversed in direction. That is to say, the action of the enclosure has not only stopped the advancing particles but reversed their momentum. This corresponds to a pressure against the enclosure represented by twice the momentum or by $2 M \Sigma (Nu^2)$.

414. Here let us pause for a moment, and consider the result to which we have been led.

Taking a plane surface perpendicular to the direction of one of the components u , and considering the molecules that were moving towards this plane, we have obtained an expression for the pressure. We find for the pressure

$$p = 2 M \Sigma (Nu^2),$$

or in other words

$$p = 2 M \{ N_1 u_1^2 + N_2 u_2^2 + \&c. \&c. \}.$$

Now had we taken a similar plane perpendicular to the component v we should have obtained another expression for the pressure as follows—

$$p = 2 M \{ N'_1 v_1^2 + N'_2 v_2^2 + \&c. \&c. \},$$

and another similar expression might be obtained for the component w . But when a gas is at rest the pressure is equal in all directions, and hence the first of these expressions must be equal to the second and the third. And not only must this be so, but likewise must N , for unit of volume (for a cubic inch for instance), be the same for v and w as for u —when v or w happens to be equal to u ; that is to say, the number of molecules in unit of volume that have

a given velocity-component in one direction is equal to the number of molecules that have the same velocity-component in any other direction.

Now the expression $M_{\Sigma} (NV^2)$ may be taken to represent for unit of volume the sum of the products of the mass of each molecule into the square of its total velocity, if we regard only those molecules that are moving towards the surface-plane, not those that are moving from it. But the square of the total velocity, or $V^2 = u^2 + v^2 + w^2$. Hence it follows that

$$M_{\Sigma} (NV^2) = M \{ N_1 u_1^2 + \&c. \} + M \{ N'_1 v_1^2 + \&c. \} \\ + M \{ N''_1 w_1^2 + \&c. \}.$$

And since from what we have just said the three right-hand expressions are equal to each other, term for term, it follows that

$$M_{\Sigma} (NV^2) = 3M(N_1 u_1^2 + \&c.) = 3M_{\Sigma}(Nu^2).$$

Hence

$$p = 2M_{\Sigma}(Nu^2) = \frac{2}{3}M_{\Sigma}(NV^2).$$

Again, the *mean square of the velocity* (Art. 410) is evidently found by dividing $M_{\Sigma} (NV^2)$ by the total mass, that is to say, calling by $\bar{V}$ the velocity of mean square,

$$\bar{V}^2 = \frac{M_{\Sigma} (NV^2)}{M_{\Sigma}(N)};$$

from which it follows that

$$p = \frac{2}{3}M_{\Sigma}(NV^2) = \frac{2}{3}M_{\Sigma}(N)\bar{V}^2.$$

Here M is of course the mass of a molecule, while $\Sigma(N)$ represents the number of molecules in unit of volume, of which the motion is at any moment towards the enclosure. But since as many are obviously moving from as towards

the enclosure, it is evident that $M\bar{v}^2(N)$ represents only half the mass in unit of volume. Hence calling ρ the density or total mass in unit of volume we have

$$p = \frac{1}{3}\rho\bar{v}^2. \quad (1)$$

Thus, while the temperature of a gas remains constant the pressure varies as the density, which is only another way of putting Boyle's law.

415. Again, if τ denotes the volume of unit of mass, we have

$$\rho = \frac{1}{\tau}. \quad \text{Hence } p\tau = \frac{1}{3}\bar{v}^2. \quad (2)$$

But the product of the pressure and the volume is proportional to the absolute temperature, as already defined in this treatise. Hence we see that the *mean square velocity and therefore the energy of agitation is proportional to the absolute temperature.*

416. Again, it has been already stated (Art. 411) that if we have the same number of molecules of two different kinds of gas existing in the same enclosure at the same temperature, then the one set will have the same kinetic energy of agitation as the other; that is to say, if M_1 , M_2 denote the mass of a molecule of each,

$$M_1\bar{v}_1^2 = M_2\bar{v}_2^2. \quad (3)$$

These two gases are now in thermal equilibrium with the sides of the enclosure and with one another. If the pressures of these two gases be called p_1 and p_2 , then from equation (1)

$$p_1 = \frac{1}{3}\rho_1\bar{v}_1^2; \quad p_2 = \frac{1}{3}\rho_2\bar{v}_2^2.$$

Now since by hypothesis we have the same number of

molecules of each gas existing in the same enclosure, the density of each will be proportional to the mass of the molecule. Hence

$$p_1 : p_2 = \rho_1 \bar{V}_1^2 : \rho_2 \bar{V}_2^2 = M_1 \bar{V}_1^2 : M_2 \bar{V}_2^2.$$

It follows from equation (3) that $p_1 = p_2$, or in other words, *at the same temperature and volume, the same number of molecules, of two different gases, will produce equal pressures.* This is the law of Gay-Lussac.

417. Again, let us suppose that at a given temperature and pressure we have equal volumes of two different gases, containing, as we have just seen, the same number of molecules of each. Now, let the temperature be increased while the pressure remains constant. It is clear that the expansion of both must be such that at the increased temperature the law of Gay-Lussac will hold, and hence the two gases will still occupy equal volumes, inasmuch as they contain the same number of molecules. In other words, *the coefficient of expansion of all gases must be the same*, which is Charles' law.

418. Besides accounting for these three great laws, the dynamical theory also indicates the laws of gaseous diffusion, gaseous viscosity, and gaseous conduction of heat. In *gaseous diffusion* we have the interchange of matter between two contiguous volumes of gas, both, let us imagine, at the same temperature and pressure, and free to mix with one another. If their chemical composition be different, it is well known that a mixture will take place. If their chemical composition be the same, there will be no perceptible change; nevertheless, according to the dynamical theory, individual particles will be constantly passing from the first to the second, while as many repass from the second to the first; but yet we are not able to perceive this, inasmuch as we cannot trace the motions of individual

particles, and the average qualities of the gas remain unaffected throughout.

419. In *gaseous viscosity* we have the interchange of momentum between two portions of gas, otherwise similar. Thus, let us imagine that we have a fixed horizontal plate, and a little above it a similar plate in oscillation,—the space between them being filled with gas. The layers of gas next the moving plate will move with it, while the layers next the fixed plate will be at rest, and the intermediate layers will have intermediate motions. Now, as the gaseous molecules pass between the moving and the fixed discs, their tendency will be to carry away part of the motion of the moving disc so as ultimately to stop it. Professor Maxwell has shewn that, according to the dynamical theory, if we keep to the same kind of gas, the same temperature, and the same motion of disc, the rate at which the motion of the moving disc is stopped will not depend on the density of the gas, but will be the same whether this be great or small. This very singular conclusion he has succeeded in proving experimentally.

420. In *gaseous conduction of heat* we have a similar exchange, not only of momentum but of molecular energy. We may suppose here that the gaseous particles ply not between a moving disc and a fixed one, but between a hot disc and a cold one, their action tending to equalise the temperatures of the two discs.

Here, as before, if we keep to similar discs with similar temperatures, and to the same kind of gas, the total carriage of heat is found by theory to be independent (within certain limits) of the density of the gas.

This conclusion has received a striking illustration by means of the experiment lately brought forward by Mr. William Crookes, in which a torsion balance with a small vertical disc at each end is suspended in a glass vessel

whose contents are almost a vacuum. In this case, if radiant heat fall upon one of the discs there is repulsion of the heated disc, which is not apparently rendered less weak however much the chamber is exhausted. It would at first sight seem that we have here some effect of radiant heat independent of the air inside. This conclusion is however not borne out when the circumstances of the case come to be examined. In the first place, Professors Tait and Dewar have shewn that the result certainly depends on the heating of one side of the disc more than the other, and that the law is that of the inverse square of the distance; and, in the next place, but previously in point of time, Professor O. Reynolds has shewn that the phenomenon follows as a result of the dynamical theory of gases. For, in virtue of gaseous conduction heat is carried from the hot disc by the particles of air to the sides of the cold glass vessel, and we have just said that the total carriage of heat is independent of the density of the residual gas. But this means that the energy of the blows struck by the gas against the disc is less than that of the return blow communicated to the gas as it leaves the disc.

Now, by the cold particles of air striking the disc it is equally bombarded on both sides, but, inasmuch as the disc is supposed to be heated only on one side, the return blows delivered by the disc to the gas will be greater on the heated side. But action and reaction being equal and opposite, there will therefore be a recession of the disc in a direction from the source of heat, and the velocity of this recession will depend upon the rate at which the disc is made by gaseous conduction to part with its excess of heat—a rate which we have just seen to be independent of the density.

421. Relations between the physical properties of bodies. Lord Kelvin and others have made some very

knocking that constitutes the pressure : also on this account they tend to intermingle with one another even against the influence of specific gravity, and it is this which constitutes gaseous diffusion. We thus see why the pressure of a gas increases when it is heated.

404. Molecular theory of gases. Here it may be well to consider some of the chief results of the theory to which allusion has just been made. For further information the reader is referred to Professor Clerk-Maxwell's book on the Theory of Heat.

The dynamical theory of gases was first suggested by Daniel Bernouilli, and was afterwards extended by Lesage, Prévost, Herapath, Joule, and Krönig, but we are indebted to Clausius and especially to Clerk-Maxwell and Boltzmann for the great development which has recently taken place. Still more recently Crookes has made important experimental investigations, while Professor O. Reynolds has added much to the theory of the subject.

405. It is assumed in this theory that all bodies consist of molecules with spaces between them of a greater or less extent. The structure of matter is thus a grained one, and we have even some reason to believe that we have been able to form a rough estimate of the size of these grains. The molecule is the smallest part of a substance that is capable of possessing all the chemical properties of the substance ; thus a molecule of chloride of sodium is still chloride of sodium, but if we suppose it to be further divided it will split up into two distinct things, namely, chlorine on the one hand, and sodium on the other. A single molecule may, and generally does, consist of various portions of matter, these being bound together by chemical forces, and bound together in a very strong way. In solids, besides the forces which bind together the various constituents of molecules, there are also strong forces, binding together the

various whole molecules, and these forces are comparable in intensity, it may be, to the forces which bind together the various parts of a single molecule—from which it follows that in solids there are definite and in general very narrow limits to the excursions of the molecules.

In liquids, however, there are fewer restrictions to such excursions, while in gases a molecule has very great freedom of motion. Therefore in a heated gas we may imagine a molecule in virtue of the motion whose energy we call heat to move a considerable distance before it encounters another molecule—in other words, to have a comparatively great free path. For the greater part of its excursion such a molecule may be supposed to move in a straight line, but ultimately it encounters either another molecule or the side of the containing vessel, and the result is a change in its motion.

406. The number of such molecules being very great it is impossible to keep a record of the varying parts of the path of any one individual, so that, in studying these encounters and their results, we must resort to the statistical method of inquiry by which we may often obtain very great knowledge of the laws that regulate communities while we are yet in profound ignorance of individual experiences.

407. Now a little consideration will render it evident that in this molecular warfare the tendency is not to a uniform distribution of velocity among the particles, and that if we imagine such a state to exist for one moment the next moment it would be destroyed. For one particle may have its velocity entirely stopped by an encounter, while another moving previously with a very great velocity may nevertheless have its velocity increased by an encounter at right-angles.

408. Nevertheless there is a tendency towards a certain average velocity among the particles, because, if we are

$= 10333 \times .089 = 919.64$ kilogrammètres for every cycle of operations. Now during each cycle it will be seen that an amount of heat equal to the latent heat of fusion of a cubic mètre of water is conveyed from the higher to the lower temperature. We thus know the quantity of heat conveyed from the source to the refrigerator as well as the quantity of work done. But we also know that this arrangement (Art. 334) cannot possibly give us more work under the circumstances than a perfect engine: in fact we shall see at last that the arrangement is a perfect engine; hence it follows that there must be a certain difference in temperature between the source and the refrigerator. This difference of temperature is easily found.

The latent heat of fusion of a kilogramme of ice (Art. 305) is 79.25 heat units, and hence that of a cubic mètre of water, or 1000 kilogrammes, will be 79,250 heat units. Multiplying by the mechanical equivalent of a heat unit, or 426 (Art. 331 a), we find the total amount of energy transferred from the higher to the lower source during a complete cycle to be 33,760,500. But we have seen that during this process mechanical energy = 919.64 is obtained. Now we know (Art. 346) that in a perfect engine the energy utilised bears to the whole energy of the heat carried from the source to the refrigerator the same proportion as the temperature-difference between the source and refrigerator does to the absolute temperature of the source.

Hence, since 273° (Art. 343) is the absolute temperature corresponding to 0°C , we have the following proportion—

$$33,760,500 : 919.64 :: 273 : \tau ; \therefore \tau = .0074^{\circ}\text{C}.$$

Now if the pressure under which the water expands into ice be doubled or become two atmospheres, twice as much work will be done by this arrangement and twice the above temperature-difference between the source and the refrigerator will be absolutely necessary; in fact, for each

atmosphere of pressure it is necessary to have a difference of $.0074^{\circ}\text{C}$. This is only another way of stating that for each atmosphere of pressure the freezing-point of ice will be reduced by $.0074^{\circ}\text{C}$. For a pressure of 16.8 atmospheres this would give $.124^{\circ}\text{C}$, a result which agrees very closely with the temperature-reduction in the freezing-point of water found experimentally by Lord Kelvin for this same pressure.

A little consideration will shew that the arrangement we have here sketched for producing work by means of the freezing of water is in reality a perfect engine.

402. Temperature. If we refer to Art. 67 of this work it will be found that the whole subject of temperature has been left in a somewhat unsatisfactory condition.

When we analyse our conception of temperature we find it to be this—

If two bodies, such as water and mercury, be brought together, and if neither parts with any of its heat to the other, then each of these two bodies is of the same temperature. If the water parts with some of its heat to the mercury, the water is said to be of a higher temperature than the mercury. On the other hand, if the water receives heat from the mercury, then the water is said to be of a lower temperature than the mercury.

It will be seen that this definition of temperature is very similar to our definition of hardness. If when two bodies are brought together *A* scratches *B*, then *A* is said to be harder than *B*; but if *B* scratches *A*, then *B* is said to be harder than *A*.

Now by means of this definition of temperature or of hardness we are quite able to construct a scale of temperature or of hardness in which we are certain that a body having a definite place in the scale shall be less hot or less hard than that above it, but more hot or more hard than

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Now by means of this definition of temperature or of hardness we are quite able to construct a scale of temperature or of hardness in which we are certain that a body having a definite place in the scale shall be less hot or less hard than that above it, but more hot or more hard than

operates upon a large volume or portion of any substance, it will produce a greater absolute change of volume than if it operated on a small volume or portion of the same substance, the ratio of the change to the original volume remaining the same in both.

Therefore in estimating elasticity we take the ratio between the increment of pressure and the proportional diminution of volume which it produces. We likewise imagine both changes to be very small.

430. The increment of pressure may be supposed to act under two different conditions—

(1) We may arrange that the temperature at the end of the process shall be the same as that before any pressure was applied.

(2) Or we may suppose that during the process of applying the pressure no heat has been allowed either to leave or enter the substance.

We shall thus have two different elasticities, the former of which corresponding to (1) we may call E_θ , and the latter of which corresponding to (2) we may call E_ϕ .

431. Again, we have in like manner two specific heats, and these are, firstly, the specific heat for constant volume, and secondly, the specific heat for constant pressure; the former of these we may call N and the latter K .

432. It is easy to show that these two specific heats are related to one another in the same manner as the two elasticities. For let us imagine a substance whose mass is unity and volume = v , to rise in temperature from t° to $t^\circ + dt$, the pressure meanwhile remaining the same. Evidently an amount of heat will be required for this process, which will be denoted by Kdt , while the proportional change of volume which takes place we may call edv . Now let the substance be suddenly compressed until it has reached its previous volume v , no heat being meanwhile

allowed either to enter the substance or to leave it. Its temperature will be evidently higher than t' , because it has received an additional amount of heat $= Kdt$. No doubt while the substance was being heated the heat had to raise a somewhat less pressure upwards than must now be applied downwards to bring it to the previous volume, so that a very small amount of additional work must be spent in order to produce compression. It will however be manifest that the heat equivalent of this work will, if we only regard small changes of pressure, be insignificant compared with Kdt , and may therefore be neglected. Now had this additional amount of heat been Ndt , it would by hypothesis have raised the substance through a temperature range $= dt$, since its volume is now the same as at first, and hence the whole increment of temperature will be found thus:—

If Ndt produce a temperature rise $= dt$, what will Kdt produce? Evidently it will produce a rise equal to $\frac{K}{N}dt$.

This compression is, let us say, attended by an increase of pressure equal to Δp . Therefore the elasticity or E_ϕ may be easily found. For the proportional change of volume is edt , and the ratio between the increment of pressure and this volume-change is $\frac{\Delta p}{edt}$. Hence by definition

$$E_\phi = \frac{\Delta p}{edt}$$

Next let the excess of temperature above $t' + dt$, which we may imagine to be now the temperature of the surrounding enclosure, be carried away. The pressure increment will now no longer be Δp , but it will be less. For if a rise in temperature $= \frac{K}{N}dt$ produce at the same volume v a pressure increment $= \Delta p$, what will a rise

of temperature equal to dt produce? Evidently it will produce $\delta p = \Delta p \times \frac{N}{K}$.

Again, the elasticity will now be E_θ , and will be denoted

by
$$\frac{\delta p}{ed t} = \frac{\Delta p}{ed t} \times \frac{N}{K}.$$

Hence
$$E_\phi : E_\theta :: \frac{\Delta p}{ed t} : \frac{\Delta p}{ed t} \times \frac{N}{K} :: K : N;$$

that is to say, the two elasticities bear to each other the same ratio as the two specific heats.

433. Let us here endeavour to find an expression for E_θ in the case of a gas of which the pressure is p , the temperature being supposed to remain constant during the compression.

Let $\frac{v_1 - v_2}{v_1}$ denote the proportional volume decrement, and $p_2 - p_1$ the pressure increment. Now by definition

$$E_\theta = \frac{\text{Pressure increment}}{\text{Prop}^l \text{ volume decrement}} = \frac{v_1(p_2 - p_1)}{v_1 - v_2} = -v \frac{\partial p}{\partial v}$$

if the changes of pressure and volume are small. But in a gas we have from Boyle's law $pv = c$ (a constant quantity when the temperature is constant). Hence on differentiation,

$$p dv + v dp = 0 \text{ or } p = -v \frac{\partial p}{\partial v}; \text{ but this is the expression}$$

already found for E_θ , or the elasticity at constant temperature. Hence in a gas $E_\theta = p$.

434. The velocity of Sound. The following method of discussing this problem is derived from that given by Professor Clerk-Maxwell in his book on the Theory of Heat. It was first introduced by the late Professor Rankine.

Let us confine ourselves to waves of longitudinal displacement; that is to say, to waves in which the motion of a particle is backwards and forwards in the direction in which the wave is travelling.

Let us further imagine that the velocity of propagation is constant, and that the wave does not alter its type as it proceeds. This last assumption means that if we could imagine ourselves to travel forward with the same velocity as that of the wave propagation, or if we could imagine the material of the wave to travel backwards with the same velocity as the wave itself travels forward, we should see no change in the appearance presented by the wave.

435. Suppose now that we have a wave of sound travelling from left to right along a rectangular tube of indefinite length and of unit section, and let us consider a plane or cross section drawn perpendicular to the direction of motion of the wave. Let u be the velocity of the air at this cross section (in the direction, let us say, from left to right). In unit of time, therefore, a column of air whose length is u passes across this imaginary plane from left to right, and since the cross section is unity, u will likewise denote the volume which passes across this plane.

Again, let v represent the volume of unit of mass of the substance, and let Q be the mass which passes across the plane in unit of time; then evidently the volume which so passes is Qv , and this must be equal to u .

436. Suppose now that while this imaginary reference plane remains fixed in space, the tube itself and all its contents are moving from right to left with a velocity U greater than u ; then evidently the mass of air which passes across the imaginary plane in unit of time in a direction from right to left will depend on the velocity $U - u$, so that if we denote this mass by Q we shall have

$$Qv = U - u. \quad (1)$$

Now let us have two such fixed reference planes A and B , and let us imagine U or the motion of the tube from right to left to be equal to the velocity of propagation of sound ;

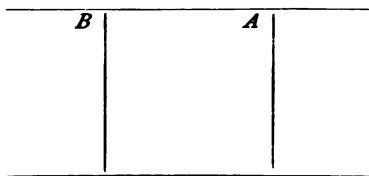


Fig. 83.

then it is evident that, inasmuch as the wave by hypothesis is of permanent type, the state of things at A and B , and hence the values of u at these planes, will always remain the same. If therefore we denote by u_A , u_B the values of u at A and B , also by v_A and p_A the volume of unit of mass and the pressure at A , and by v_B , p_B the corresponding values of these elements at B , we shall have

$$Q_A v_A = U - u_A. \quad (2)$$

$$Q_B v_B = U - u_B. \quad (3)$$

437. Again, it is evident that in consequence of the wave being of constant type, the density at all points between the fixed imaginary planes A and B remains the same, and hence the mass of matter embraced between these two planes remains the same. It follows that the mass which enters in unit of time at A must be equal to that which leaves the space at B , or in other words

$$Q_A = Q_B = Q \text{ (let us say)}. \quad (4)$$

Hence also from equations (2) and (3)

$$u_A = U - Q v_A. \quad (5)$$

$$u_B = U - Q v_B. \quad (6)$$

But while in unit of time a mass Q enters at A and an

equal mass leaves the interval at B , yet the mass which enters at A has a velocity $U - u_A$, while that which leaves at B has a velocity $U - u_B$. If u_A be greater than u_B , it follows that the momentum (from right to left) of the entering fluid is less than that of the issuing fluid by the amount $Q\{u_A - u_B\}$.

438. Now it is evident that this difference in the momentum of the air which enters and departs from the interval must be wholly due to the difference of the pressures at A and B , and must be measured by this difference; and since the fluid issues from B with a greater momentum from right to left than it enters at A , the pressure at A must be greater than the pressure at B in order thus to increase the momentum of the fluid as it passes from A to B . We thus obtain

$$p_A - p_B = Q\{u_A - u_B\} \quad (7)$$

Substituting the values of u_A and u_B from equations (5) and (6) we obtain

$$p_A - p_B = Q^2\{v_B - v_A\}.$$

Hence

$$p_A + Q^2 v_A = p_B + Q^2 v_B. \quad (9)$$

Now since A and B may be any planes whatever, it follows that the quantity $p + Q^2 v$ must continue constant. If we call this quantity P , we have $p + Q^2 v = P$, and hence

$$p = P - Q^2 v. \quad (10)$$

439. Let us now suppose that in the wave under consideration the changes of volume and pressure are comparatively small, that is to say, $p_A - p_B$ or δp , and $v_B - v_A$ or δv , are small compared to p and v . Now by the definition of elasticity (Art. 429)

$$E = v \frac{p_A - p_B}{v_B - v_A} = v Q^2 \text{ (by equation (8)).} \quad (11)$$

Again, if v is the volume of unit of mass for those portions

of air which are not disturbed by the wave, and where $s=0$. we have from equation (2)

$$U = Qr. \quad (12)$$

Hence

$$U^2 = Q^2 r^2 = Er \text{ (by equation (11))}; \quad (13)$$

that is to say, the square of the velocity of propagation of a wave of sound in air or any substance is equal to the product of the elasticity and of the volume of unit of mass.

Here it is evident that the elasticity must be that of sudden compression, since the motions which constitute sound are quickly performed, and we may suppose that during the process no heat is allowed to escape. Hence

$$U^2 = E_s r.$$

440. If we denote by γ the ratio between the two elasticities or the two specific heats for air, we shall have (Art. 433)

$$E_s = \gamma E_o = \gamma p. \quad (14)$$

Hence (equation (13))

$$U^2 = \gamma p v. \quad (15)$$

Now since pv remains constant (Art 60) while the temperature is the same, it is evident that the velocity of sound in the same gas and at the same temperature is independent of the pressure.

Again, since pv (Arts. 136, 343) is proportional to the absolute temperature, it is evident that the velocity is proportional to the square root of the absolute temperature.

441. So long therefore as the temperature is the same, the velocity at which sound proceeds through the atmosphere is the same at all elevations; but when (as is generally the case, particularly during calm clear days) there is an upward diminution of temperature, there will be a corresponding diminution in the velocity of sound at different elevations.

Professor Reynolds has shown that this variation in the velocity of sound at different elevations must, when the

diminution of temperature is upwards, cause the sound, which would otherwise proceed horizontally along the earth's surface, to leave the surface and move in an upward direction to an extent depending on the variation of temperature; and that we thus have an explanation of the greater distances at which sounds can be heard on cloudy as compared with clear days, and particularly during the night as compared with the day.

442. In order to utilise equation (15) for determining the velocity of sound, let us conceive of a homogeneous atmosphere extending upwards, the density always remaining the same as the actual density at the earth's surface. Now let H denote the height of this atmosphere, the weight of which will produce a pressure equal to the actual pressure or p , and let the cross section of the column we are considering be unity. The volume of this column will thus be H , and if v be the volume of unit of mass and m the whole mass of the column, then

$$H = mv. \quad (16)$$

Again, the pressure produced by the column is $p = mg$ where g is the intensity of gravity. Hence

$$pv = mgv = Hg \text{ (by equation (16)).} \quad (17)$$

Therefore

$$U^2 = \gamma pv = g\gamma H. \quad (18)$$

443. It appears from equation (18) that if we know the value of the intensity of gravity, the ratio between the two specific heats, and the height of the homogeneous atmosphere, we can determine the velocity of sound, or conversely, if we know the velocity of sound, the intensity of gravity, and the height of the homogeneous atmosphere, we can determine the ratio between the two specific heats.

This last may be done as follows:—We know (Art. 149) that the mass of one cubic mètre of atmospheric air at

°C and at the pressure of 760 reduced millimetres of mercury is 1.293187 kilogrammes, and that this pressure is (Art. 332) equivalent to 10333 kilogrammes' weight per square mètre. Hence, in order to produce this pressure by the weight of the air alone, we should require a column

$$\frac{10333}{1.293187} = 7990 \text{ mètres in height.}$$

Again, the acceleration produced by gravity or $g = 32.2$ feet or 9.815 mètres per second per second. Also the velocity of sound in air at °C is found by experiment to be 332.2 mètres per second.

Now $(332.2)^2 = 110357$, and hence γ or

$$\frac{U^2}{gH} = \frac{110357}{9.815 \times 7990} = 1.408.$$

This then is the ratio between the two elasticities or the two specific heats for air.

But we have seen from Art. 332 that the same ratio independently determined by a totally different experiment is $\frac{83.51}{59.25} = 1.409$. It will thus be seen that the two

determinations agree together very well.

444. Graphical Representations of Physical Laws.

By means of a series of isothermal lines we may conveniently express the relations which hold between the volume, the pressure, and the temperature in a perfect gas.

Suppose for instance that our ordinates represent pressures and our abscissæ volumes, then, if we suppose the temperature of the gas to remain constant, we may express as in Fig. 84, by means of a curve, the relation between the pressure and the volume.

The relation is such that the product of the pressure into the volume is constant, and hence the curve is that known as the rectangular hyperbola.

If, however, we alter the temperature of our gas we must then employ another curved line to express the new relation between the pressure and the volume. This curve will, as before, be a rectangular hyperbola, but it will lie entirely above the previous curve if the temperature has been increased, and entirely below it if the temperature has been diminished.

The various hyperbolic curves are thus seen to constitute

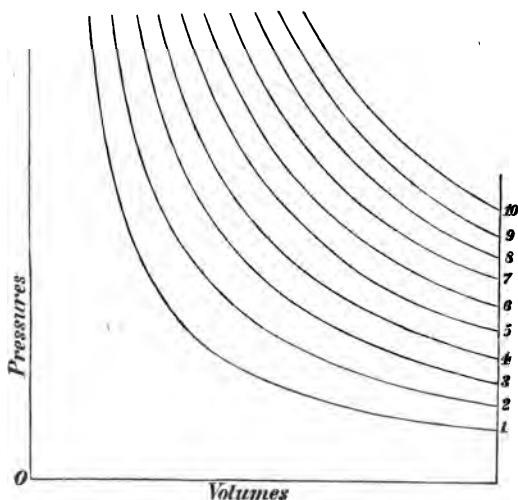


Fig. 84.

a series of isothermal lines corresponding to different temperatures, each one expressing the relation between the volume and the pressure of the gas corresponding to its own temperature.

Now it is easily seen from Boyle's and Charles' laws taken together that

$$pv = C(1 + at);$$

and hence the product pv will as the temperature increases

receive increments proportional to the increment of temperature.

It follows that if while the temperature regularly increases the volume be kept constant the pressure will receive increments proportional to the increment of temperature, and hence if we draw a series of isothermals corresponding to regular intervals of temperature and cut them by means of a vertical line, as in the figure, the distance between the points at which this line cuts any two neighbouring isothermals will be the same. Thus the distance between 1 and 2 is equal to that between 2 and 3 or that between 3 and 4, and so on.

445. Let us now suppose that instead of a perfect gas we consider a quantity of superheated steam, which is contained in a cylinder in which a steam-tight piston works. By pressing down the piston we increase the pressure of the steam. If we imagine that during the operation the temperature is kept the same, and that this temperature is considerably above the point of saturation corresponding to the initial pressure, then for the first part of the compression the steam may be regarded as a nearly perfect gas and its isothermal curve will not greatly differ from the rectangular hyperbola.

When however a pressure has been attained nearly equal to the maximum pressure which corresponds to the temperature of the steam, there will be a departure from Boyle's law (Art. 148), and this will be in such a direction that the pressure will increase less rapidly on account of diminution of volume than it would have done if Boyle's law had been obeyed.

When the maximum pressure has been attained, any further diminution of volume will not at first increase the pressure, but will only condense some of the steam into water. The isothermal curve will now become a hori-

zontal line, diminution of volume being so far unaccompanied by any sensible increase of pressure, and things will remain so until the volume has been reduced so far as to leave no vacant steam-space above the water into which the whole of the original steam has now been condensed. It is clear that henceforth any further diminution of volume will be resisted by that very powerful force which water opposes to any attempt to diminish its volume, and hence very small diminutions of volume will now correspond to very great increments of pressure—in other words, the isothermal curve will now become nearly vertical. It thus appears that the isothermal of steam, or of a mixture of steam and water, is first of all a curve which approximates to a rectangular hyperbola, then a horizontal line, and finally a line approximately vertical.

446. In a previous part of this work (Art. 131) the researches of Dr. Andrews on carbonic acid have been alluded to, and we have stated the conclusion arrived at by that experimentalist, namely, that matter may be made to pass from the gaseous into the liquid state by a series of gradations so gentle that the passage shall nowhere present any interruption or breach of continuity.

The following diagram, taken from Dr. Andrews' paper and from Professor Maxwell's book on Heat, will exhibit graphically the reasoning which led to this conclusion. Here at first, and corresponding to comparatively low temperatures, such as 13.1°C , we have an isothermal very analogous to that already mentioned as characterising a mixture of steam and water. When however the temperature is increased this likeness gradually disappears, until at such temperatures as 48.1°C we have a line exhibiting all the properties of the isothermal belonging to a perfect gas, and denoting that however much we may increase the pressure, we shall never at this temperature obtain the

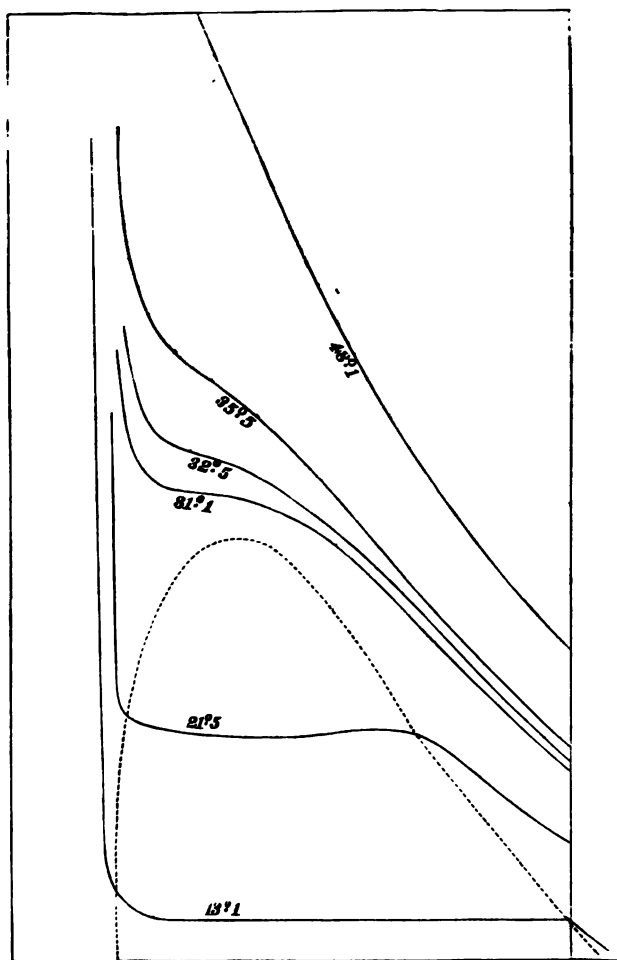
*Isothermals of Carbonic Acid*

Fig. 85.

liquid in contact with its own gas. Thus at comparatively low temperatures there is a range of volume throughout which the substance CO_2 is capable of appearing together in its two states, this range beginning with the point at which condensation begins and ending with that at which all the gas has been condensed into liquid.

Now, if a line (dotted in Fig. 85) be drawn through these two points for the various temperatures, it will be found that as the temperature rises the distance between the points at which the isothermal cuts this dotted curve will diminish, or in other words, the range of volume between the point at which condensation begins, and that at which all the gas is entirely condensed, will diminish as the temperature increases. At some temperature these two points will merge into one, and therefore at this temperature there will be no distinction between saturated gas and liquid, or in other words, we shall have the coalescence of the gaseous and liquid states. This therefore is the critical point of Dr. Andrews, who in his experiments determined it to take place at the temperature 30.92°C and at the pressure of from 73 to 75 atmospheres.

In Dr. Andrews' diagram the lower isothermals do not exactly correspond with the description in Art. 445, for neither are their middle portions horizontal, nor do the portions representing the liquid and gaseous conditions break off abruptly from the middle portions. The reason is that the experimental tube contained a little air as well as carbonic acid, so that the registered pressures are not those of CO_2 alone.

447. In 1873 Professor James Thomson discussed with the aid of a diagram certain relations between the Gaseous, the Liquid, and the Solid states of Water-Substance. His reasoning is as follows.

If we take any substance which we can have in the three

states, gaseous, liquid, and solid, it will be found that whenever any two of these states are present in contact together the pressure and temperature are dependent on each other, so that when one is given the other is fixed. Thus in Fig. 34 (Art. 141) we have a curve exhibiting in its upper part the relation between the temperature and pressure when water and steam exist together, and in its lower part the relation between the temperature and pressure when ice and steam exist together.

In addition to these we may have a third curve exhibiting the same relation when water and ice exist together, inasmuch as we know that the melting-point of ice depends upon the pressure. It would appear to result from this that these three curves must cross one another in one point and only one. To make this reasoning clear let us consider an ordinary case of ice and water at 0°C at the usual atmospheric pressure. May it not be said that here we have the three states of water substance together—namely, aqueous vapour, water, and ice? Unquestionably we have these three states side by side, but it is manifest that the atmospheric pressure does not represent the pressure of saturated vapour at the temperature of the experiment. But if we now reduce the pressure to that of saturated aqueous vapour at 0°C we raise by the same means the melting-point of the ice, so that the water in the experiment will gradually become ice. This prepares us to acknowledge that there is one point, and only one, where the three curves above mentioned can exist together, and therefore cut one another, and this is called by Professor James Thomson the triple point.

448. In Fig. 86 the ice-steam line is denoted by *NTQ*, the water-steam line by *PTL*, and the ice-water line by *MTR*, *T* being the triple point at which these three lines meet.

The first two of these lines have generally been regarded as one, and Regnault, we have already remarked (Art 145), was of opinion that his curve showed no peculiarity about this point. Nevertheless Professor Kirchhoff in 1858 and Professor James Thomson in 1871 were led, on different grounds and quite independently of each other, to believe that the ice-steam and water-steam lines are, in reality,

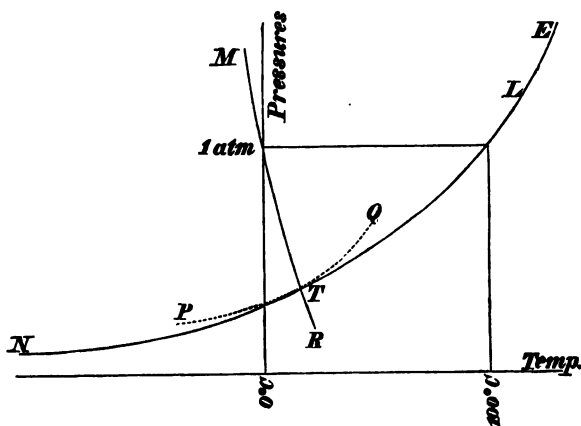


Fig. 86.

two distinct curves, crossing each other with a re-entrant angle at T .

The argument employed by the latter rests on the formula of Art. 341, viz. $\frac{\partial p}{\partial t} = \frac{M}{\phi(t)}$, where $\phi(t)$ represents a function which depends only upon the temperature, and is independent of the nature of the substance used. The substance need not even be homogeneous throughout, but it may be heterogeneous, as, for instance, a mass of water and steam, or ice and water, or ice and steam; in these cases, however,

140. Let us now consider the ice-steam curve, and have at t_1' and t_2' denote the altered values of the above expressions when we have ice instead of water: then we deduce, as before

$$\frac{t_2'}{t_1'} = \frac{I'}{I}.$$

141. Now $\frac{t_2'}{t_1'}$ denotes the pressure rise of the water-steam curve for one degree centigrade above the triple point, and $\frac{t_2'}{t_1'}$ denotes the corresponding rise of the ice-steam curve.

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It follows that if the curves are really the same, then $\frac{dp}{dt} = \frac{dp'}{dt}$, and hence $M = M'$.

But, on the other hand, if we have reason to believe that M and M' are different, then evidently the two curves are not the same.

Now M (Art. 337) denotes the rate at which heat must be supplied to a substance consisting of steam and water at the triple point (per unit augmentation of volume of the heterogeneous body) so as to let it expand without varying in temperature. During the expansion a certain mass of water will evaporate and assume the gaseous condition.

M' , on the other hand, denotes the corresponding rate for a substance consisting of steam and ice, and here during a similar expansion practically the same mass of ice as before of water will evaporate and assume the gaseous condition.

The amounts of heat required in these two cases will thus bear the same proportion to each other as the heat required to evaporate one kilogramme of water bears to that required to evaporate one kilogramme of ice. Now, according to Regnault (Art. 308), the latent heat of evaporation of water at 0°C (the triple point nearly) is 606.5, while in the case of ice we have to add to this the latent heat of water, or 79.25 (Art. 306).

Therefore at this point the ratio

$$\frac{M}{M'} = \frac{606.5}{79.25 + 606.5} = \frac{1}{1.13}, \text{ and hence } \frac{\frac{dp}{dt}}{\frac{dp'}{dt}} = \frac{1}{1.13}.$$

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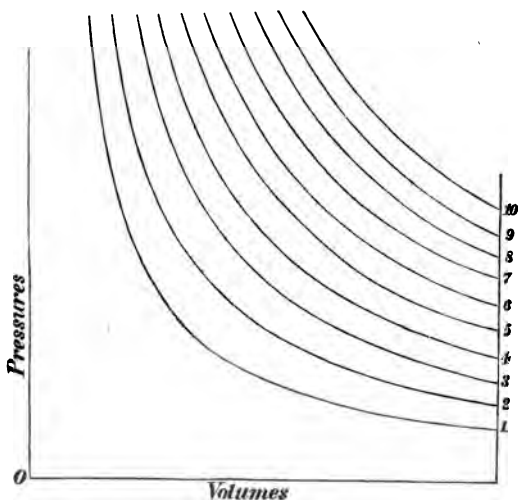


Fig. 84.

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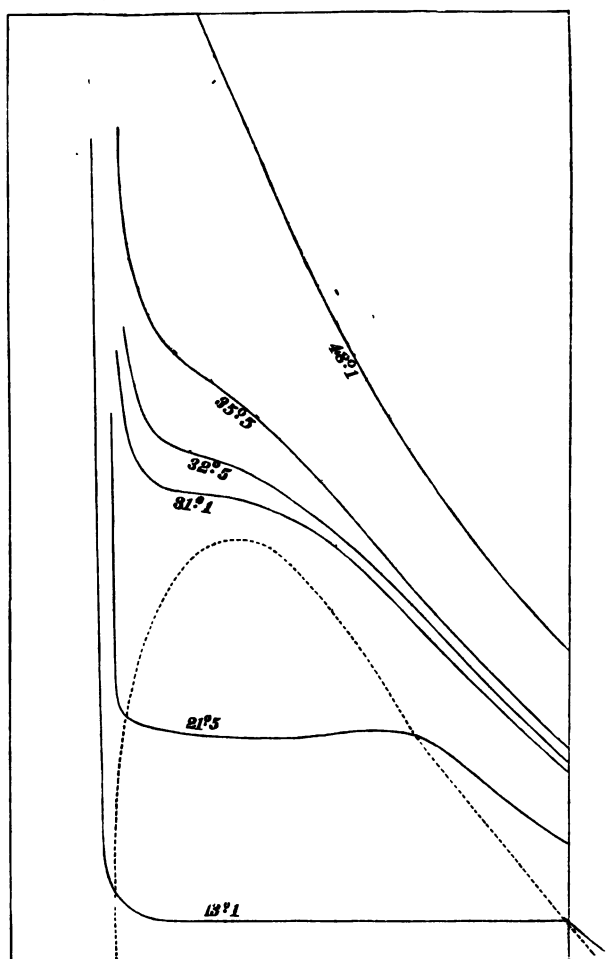
*Isothermals of Carbonic Acid*

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In addition to these we may have a third curve exhibiting the same relation when water and ice exist together, inasmuch as we know that the melting-point of ice depends upon the pressure. It would appear to result from this that these three curves must cross one another in one point and only one. To make this reasoning clear let us consider an ordinary case of ice and water at 0°C at the usual atmospheric pressure. May it not be said that here we have the three states of water substance together—namely, aqueous vapour, water, and ice? Unquestionably we have these three states side by side, but it is manifest that the atmospheric pressure does not represent the pressure of saturated vapour at the temperature of the experiment. But if we now reduce the pressure to that of saturated aqueous vapour at 0°C we raise by the same means the melting-point of the ice, so that the water in the experiment will gradually become ice. This prepares us to acknowledge that there is one point, and only one, where the three curves above mentioned can exist together, and therefore cut one another, and this is called by Professor James Thomson the triple point.

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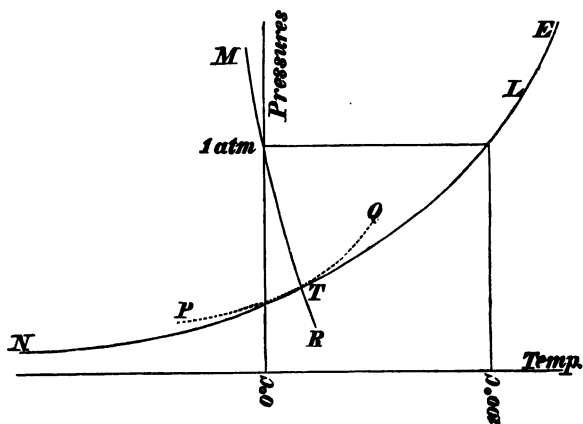


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two distinct curves, crossing each other with a re-entrant angle at T .

The argument employed by the latter rests on the formula of Art. 341, viz. $\frac{\partial p}{\partial t} = \frac{M}{\phi(t)}$, where $\phi(t)$ represents a function which depends only upon the temperature, and is independent of the nature of the substance used. The substance need not even be homogeneous throughout, but it may be heterogeneous, as, for instance, a mass of water and steam, or ice and water, or ice and steam; in these cases, however,

it is not necessary to keep the volume constant in estimating $\frac{\partial p}{\partial t}$, inasmuch as for such mixtures the mere change of volume does not affect the pressure, and this constancy of volume is therefore not essential, so that for $\frac{\partial p}{\partial t}$ (where ∂ denotes partial differentiation with v constant) we may write $\frac{dp}{dt}$, which implies constancy of nothing but the mixed—or, as it is called, *saturated*—condition of the substance.

449. Now, let us apply this formula first to steam with water and then to steam with ice, at the temperature of the triple point, or, which is sufficiently near it, at the temperature 0°C .

Beginning with a mixture of saturated steam and water, let $\frac{dp}{dt}$ denote the rate of increase of pressure for unit increase of temperature. Then $\frac{dp}{dt} = \frac{M}{\phi(t)}$.

450. Let us next consider the ice-steam curve, and here let $\frac{dp'}{dt}$ and M' denote the altered values of the above expressions when we have ice instead of water; then, as before, we have

$$\frac{dp'}{dt} = \frac{M'}{\phi(t)}.$$

$$\text{Hence it follows that } \frac{\frac{dp}{dt}}{\frac{dp'}{dt}} = \frac{M}{M'}.$$

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It follows that if the curves are really the same, then $\frac{dp}{dt} = \frac{dp'}{dt}$, and hence $M = M'$.

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Now M (Art. 337) denotes the rate at which heat must be supplied to a substance consisting of steam and water at the triple point (per unit augmentation of volume of the heterogeneous body) so as to let it expand without varying in temperature. During the expansion a certain mass of water will evaporate and assume the gaseous condition.

M' , on the other hand, denotes the corresponding rate for a substance consisting of steam and ice, and here during a similar expansion practically the same mass of ice as before of water will evaporate and assume the gaseous condition.

The amounts of heat required in these two cases will thus bear the same proportion to each other as the heat required to evaporate one kilogramme of water bears to that required to evaporate one kilogramme of ice. Now, according to Regnault (Art. 308), the latent heat of evaporation of water at 0°C (the triple point nearly) is 606.5, while in the case of ice we have to add to this the latent heat of water, or 79.25 (Art. 306).

Therefore at this point the ratio

$$\frac{M}{M'} = \frac{606.5}{79.25 + 606.5} = \frac{1}{1.13}, \text{ and hence } \frac{\frac{dp}{dt}}{\frac{dp'}{dt}} = \frac{1}{1.13}.$$

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452. Professor James Thomson finds by reference to Regnault's original memoir that while constructing his tables of the pressure of aqueous vapour he made use of two formulæ, (D) and (E), of which (D) may be regarded as the formula for giving the pressure p of steam with water, and

E as that for giving the pressure p' of steam with ice. The following tables are derived from these two formulæ:—

By formula (D). Steam with water.

Temperatures.	Pressures = p .	Differences for 1° which are values of $\frac{dp}{dt}$ for intermediate temperatures.	Temperatures to which the values of $\frac{dp}{dt}$ belong.
-3°	3.703	} .280 } .298 } .319 } .340 } .362 } .385	$-2\frac{1}{2}^\circ$
-2°	3.983		$-1\frac{1}{2}^\circ$
-1°	4.281		$-\frac{1}{2}^\circ$
0°	4.600		$+\frac{1}{2}^\circ$
$+1^\circ$	4.940		$+1\frac{1}{2}^\circ$
$+2^\circ$	5.302		$+2\frac{1}{2}^\circ$
$+3^\circ$	5.687		

By formula (E). Steam with ice.

Temperatures.	Pressures = p' .	Differences for 1° which are values of $\frac{dp'}{dt}$ for intermediate temperatures.	Temperatures to which the values of $\frac{dp'}{dt}$ belong.
-3°	3.644	} .297 } .322 } .347 } .375 } .405 } .437	$-2\frac{1}{2}^\circ$
-2°	3.941		$-1\frac{1}{2}^\circ$
-1°	4.263		$-\frac{1}{2}^\circ$
0°	4.610		$+\frac{1}{2}^\circ$
$+1^\circ$	4.985		$+1\frac{1}{2}^\circ$
$+2^\circ$	5.390		$+2\frac{1}{2}^\circ$
$+3^\circ$	5.827		

453. From these two tables the following results are deduced :—

Temperatures.	Values deduced for $\frac{dp'}{\frac{dt}{dp}}$
$-2\frac{1}{2}^{\circ}$	$\frac{297}{280} = 1.06$
$-1\frac{1}{2}^{\circ}$	$\frac{322}{298} = 1.08$
$-\frac{1}{2}^{\circ}$	$\frac{347}{319} = 1.09$
$+\frac{1}{2}^{\circ}$	$\frac{375}{340} = 1.10$
$+1\frac{1}{2}^{\circ}$	$\frac{405}{362} = 1.12$
$+2\frac{1}{2}^{\circ}$	$\frac{437}{385} = 1.13$

giving a mean value of about 1.10, which is not far different from the value 1.13, which theory indicates.

A recent research by Messrs. Ramsay and Young indicates that similar laws hold for other substances.

TABLE I.

Shewing the pressure of aqueous vapour in inches of mercury at the latitude 53° 21' for each degree Fahr. from -30° to 432°.

Temperature.	Pressure in in. of mercury at 32° at sea level. (Lat. 53° 21'.)	Temperature.	Pressure in in. of mercury at 32° at sea level. (Lat. 53° 21'.)	Temperature.	Pressure in in. of mercury at 32° at sea level. (Lat. 53° 21'.)
0	in.	0	in.	0	in.
-30	0.0099	+ 1	0.0459	+ 32	0.1810
29	0.0105	2	0.0481		
28	0.0111	3	0.0503	32	0.1810
27	0.0117	4	0.0526	33	0.1883
26	0.0123	5	0.0551	34	0.1959
25	0.0130	6	0.0576	35	0.2038
24	0.0137	7	0.0603	36	0.2119
23	0.0144	8	0.0630	37	0.2204
22	0.0152	9	0.0659	38	0.2291
21	0.0160	10	0.0689	39	0.2381
20	0.0168	11	0.0721	40	0.2475
19	0.0177	12	0.0753	41	0.2571
18	0.0186	13	0.0788	42	0.2672
17	0.0196	14	0.0823	43	0.2775
16	0.0206	15	0.0861	44	0.2882
15	0.0216	16	0.0899	45	0.2993
14	0.0227	17	0.0940	46	0.3108
13	0.0238	18	0.0982	47	0.3226
12	0.0250	19	0.1027	48	0.3349
11	0.0262	20	0.1073	49	0.3476
10	0.0275	21	0.1121	50	0.3607
9	0.0289	22	0.1171	51	0.3742
8	0.0303	23	0.1223	52	0.3882
7	0.0317	24	0.1278	53	0.4026
6	0.0332	25	0.1335	54	0.4175
5	0.0348	26	0.1395	55	0.4329
4	0.0365	27	0.1457	56	0.4488
3	0.0382	28	0.1522	57	0.4653
2	0.0400	29	0.1589	58	0.4822
1	0.0419	30	0.1660	59	0.4997
0	0.0439	31	0.1733	60	0.5178

of Aqueous Vapour.

45I

Temperature.	Pressure in in. of mercury at 32° at sea level. (Lat. 53° 21'.)	Temperature.	Pressure in in. of mercury at 32° at sea level. (Lat. 53° 21'.)	Temperature.	Pressure in in. of mercury at 32° at sea level. (Lat. 53° 21'.)
o	in.	o	in.	o	in.
61	0.5364	106	2.292	151	7.729
62	0.5556	107	2.360	152	7.922
63	0.5755	108	2.430	153	8.120
64	0.5959	109	2.502	154	8.321
65	0.6170	110	2.576	155	8.527
66	0.6388	111	2.652	156	8.737
67	0.6612	112	2.729	157	8.951
68	0.6843	113	2.809	158	9.170
69	0.7081	114	2.890	159	9.393
70	0.7327	115	2.974	160	9.621
71	0.7580	116	3.059	161	9.853
72	0.7841	117	3.147	162	10.090
73	0.8109	118	3.237	163	10.332
74	0.8386	119	3.329	164	10.579
75	0.8671	120	3.423	165	10.831
76	0.8964	121	3.520	166	11.088
77	0.9266	122	3.619	167	11.350
78	0.9577	123	3.720	168	11.617
79	0.9898	124	3.824	169	11.889
80	1.0227	125	3.930	170	12.167
81	1.0566	126	4.039	171	12.450
82	1.0915	127	4.150	172	12.739
83	1.1274	128	4.264	173	13.033
84	1.1643	129	4.381	174	13.333
85	1.2023	130	4.500	175	13.639
86	1.2413	131	4.622	176	13.951
87	1.2815	132	4.747	177	14.268
88	1.3228	133	4.874	178	14.592
89	1.3652	134	5.005	179	14.922
90	1.4088	135	5.139	180	15.258
91	1.4537	136	5.275	181	15.600
92	1.4998	137	5.415	182	15.949
93	1.5471	138	5.558	183	16.304
94	1.5958	139	5.704	184	16.666
95	1.6457	140	5.854	185	17.034
96	1.6971	141	6.006	186	17.410
97	1.7498	142	6.162	187	17.792
98	1.8039	143	6.322	188	18.181
99	1.8595	144	6.485	189	18.577
100	1.917	145	6.651	190	18.981
101	1.975	146	6.822	191	19.392
102	2.035	147	6.996	192	19.810
103	2.097	148	7.173	193	20.236
104	2.160	149	7.354	194	20.669
105	2.225	150	7.540	195	21.110

Temperature.	Pressure in in. of mercury at 32° at sea level. (Lat. 53° 21'.)	Temperature.	Pressure in in. of mercury at 32° at sea level. (Lat. 53° 21'.)	Temperature.	Pressure in in. of mercury at 32° at sea level. (Lat. 53° 21'.)
°	in.	°	in.	°	in.
196	21.559	241	51.78	286	110.32
197	22.016	242	52.72	287	112.05
198	22.480	243	53.67	288	113.81
199	22.953	244	54.64	289	115.60
200	23.435	245	55.63	290	117.40
201	23.924	246	56.62	291	119.23
202	24.422	247	57.64	292	121.08
203	24.929	248	58.66	293	122.95
204	25.445	249	59.71	294	124.85
205	25.969	250	60.76	295	126.77
206	26.502	251	61.84	296	128.71
207	27.045	252	62.92	297	130.68
208	27.597	253	64.03	298	132.67
209	28.158	254	65.15	299	134.68
210	28.728	255	66.28	300	136.72
211	29.308	256	67.43	301	138.79
212	29.898	257	68.60	302	140.88
213	30.50	258	69.79	303	142.99
214	31.11	259	70.99	304	145.13
215	31.73	260	72.20	305	147.30
216	32.35	261	73.44	306	149.49
217	32.99	262	74.69	307	151.70
218	33.64	263	75.96	308	153.95
219	34.30	264	77.24	309	156.22
220	34.98	265	78.55	310	158.51
221	35.66	266	79.87	311	160.83
222	36.35	267	81.21	312	163.18
223	37.05	268	82.56	313	165.56
224	37.77	269	83.94	314	167.97
225	38.50	270	85.33	315	170.40
226	39.23	271	86.75	316	172.86
227	39.98	272	88.18	317	175.35
228	40.74	273	89.63	318	177.86
229	41.52	274	91.10	319	180.41
230	42.30	275	92.59	320	182.98
231	43.10	276	94.10	321	185.59
232	43.91	277	95.63	322	188.22
233	44.73	278	97.18	323	190.88
234	45.57	279	98.75	324	193.57
235	46.42	280	100.34	325	196.29
236	47.28	281	101.95	326	199.05
237	48.15	282	103.58	327	201.83
238	49.04	283	105.23	328	204.64
239	49.94	284	106.91	329	207.49
240	50.85	285	108.60	330	210.36

Tempe- rature.	Pressure in in. of mercury at 32° at sea level. (Lat. 53° 21'.)	Tempe- rature.	Pressure in in. of mercury at 32° at sea level. (Lat. 53° 21'.)	Tempe- rature.	Pressure in in. of mercury at 32° at sea level. (Lat. 53° 21'.)
°	in.	°	in.	°	in.
331	213.27	365	332.52	399	498.22
332	216.21	366	336.68	400	503.90
333	219.18	367	340.88	401	509.63
334	222.18	368	345.13	402	515.41
335	225.21	369	349.41	403	521.24
336	228.28	370	353.73	404	527.12
337	231.38	371	358.10	405	533.06
338	235.51	372	362.50	406	539.04
339	237.68	373	366.95	407	545.07
340	240.88	374	371.44	408	551.16
341	244.12	375	375.98	409	557.30
342	247.38	376	380.55	410	563.48
343	250.69	377	385.17	411	569.73
344	254.02	378	389.84	412	576.02
345	257.39	379	394.54	413	582.36
346	260.80	380	399.29	414	588.76
347	264.24	381	404.09	415	595.22
348	267.72	382	408.92	416	601.72
349	271.23	383	413.81	417	608.28
350	274.78	384	418.73	418	614.90
351	278.37	385	423.71	419	621.56
352	281.99	386	428.73	420	628.29
353	285.65	387	433.79	421	635.07
354	289.35	388	438.90	422	641.90
355	293.08	389	444.06	423	648.79
356	296.85	390	449.26	424	655.73
357	300.66	391	454.51	425	662.73
358	304.51	392	459.80	426	669.79
359	308.39	393	465.15	427	676.90
360	312.32	394	470.54	428	684.07
361	316.28	395	475.98	429	691.30
362	320.28	396	481.46	430	698.58
363	324.32	397	487.00	431	705.92
364	328.40	398	492.58	432	713.32

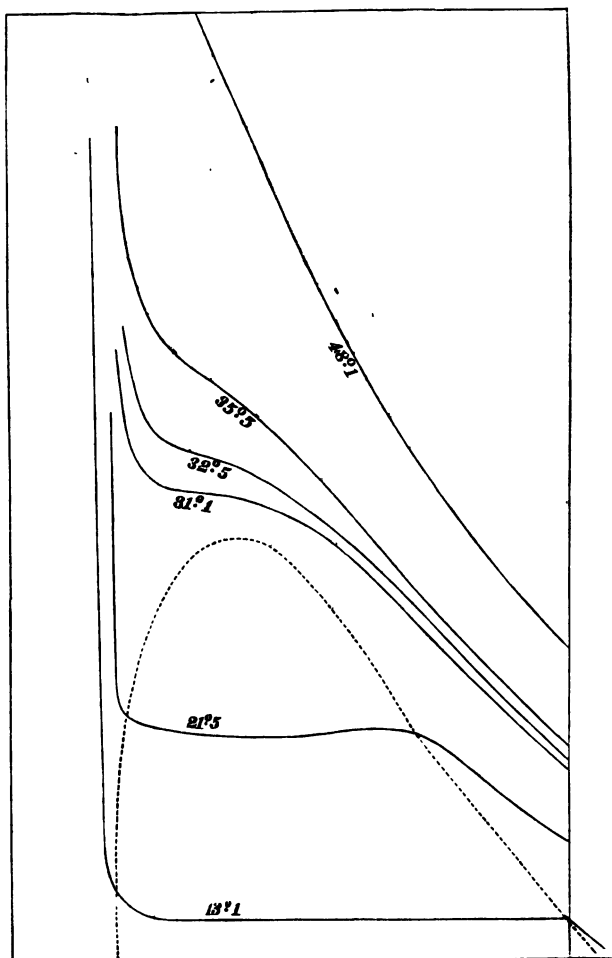
*Isothermals of Carbonic Acid*

Fig. 85.

liquid in contact with its own gas. Thus at comparatively low temperatures there is a range of volume throughout which the substance CO_2 is capable of appearing together in its two states, this range beginning with the point at which condensation begins and ending with that at which all the gas has been condensed into liquid.

Now, if a line (dotted in Fig. 85) be drawn through these two points for the various temperatures, it will be found that as the temperature rises the distance between the points at which the isothermal cuts this dotted curve will diminish, or in other words, the range of volume between the point at which condensation begins, and that at which all the gas is entirely condensed, will diminish as the temperature increases. At some temperature these two points will merge into one, and therefore at this temperature there will be no distinction between saturated gas and liquid, or in other words, we shall have the coalescence of the gaseous and liquid states. This therefore is the critical point of Dr. Andrews, who in his experiments determined it to take place at the temperature 30.92°C and at the pressure of from 73 to 75 atmospheres.

In Dr. Andrews' diagram the lower isothermals do not exactly correspond with the description in Art. 445, for neither are their middle portions horizontal, nor do the portions representing the liquid and gaseous conditions break off abruptly from the middle portions. The reason is that the experimental tube contained a little air as well as carbonic acid, so that the registered pressures are not those of CO_2 alone.

447. In 1873 Professor James Thomson discussed with the aid of a diagram certain relations between the Gaseous, the Liquid, and the Solid states of Water-Substance. His reasoning is as follows.

If we take any substance which we can have in the three

states, gaseous, liquid, and solid, it will be found that whenever any two of these states are present in contact together the pressure and temperature are dependent on each other, so that when one is given the other is fixed. Thus in Fig. 34 (Art. 141) we have a curve exhibiting in its upper part the relation between the temperature and pressure when water and steam exist together, and in its lower part the relation between the temperature and pressure when ice and steam exist together.

In addition to these we may have a third curve exhibiting the same relation when water and ice exist together, inasmuch as we know that the melting-point of ice depends upon the pressure. It would appear to result from this that these three curves must cross one another in one point and only one. To make this reasoning clear let us consider an ordinary case of ice and water at 0°C at the usual atmospheric pressure. May it not be said that here we have the three states of water substance together—namely, aqueous vapour, water, and ice? Unquestionably we have these three states side by side, but it is manifest that the atmospheric pressure does not represent the pressure of saturated vapour at the temperature of the experiment. But if we now reduce the pressure to that of saturated aqueous vapour at 0°C we raise by the same means the melting-point of the ice, so that the water in the experiment will gradually become ice. This prepares us to acknowledge that there is one point, and only one, where the three curves above mentioned can exist together, and therefore cut one another, and this is called by Professor James Thomson the triple point.

448. In Fig. 86 the ice-steam line is denoted by *NTQ*, the water-steam line by *PTL*, and the ice-water line by *MTR*, *T* being the triple point at which these three lines meet.

The first two of these lines have generally been regarded as one, and Regnault, we have already remarked (Art 145), was of opinion that his curve showed no peculiarity about this point. Nevertheless Professor Kirchhoff in 1858 and Professor James Thomson in 1871 were led, on different grounds and quite independently of each other, to believe that the ice-steam and water-steam lines are, in reality,

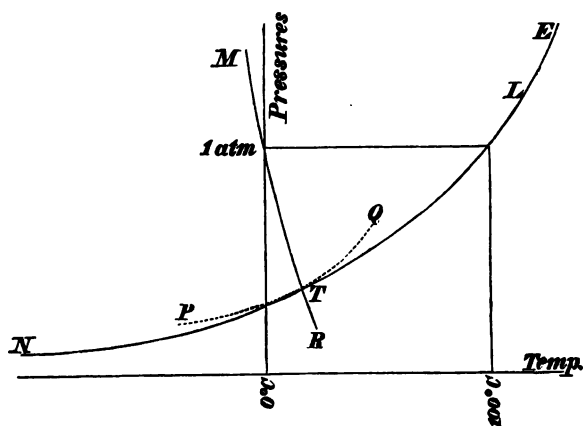


Fig. 86.

two distinct curves, crossing each other with a re-entrant angle at T .

The argument employed by the latter rests on the formula of Art. 341, viz. $\frac{\partial p}{\partial t} = \frac{M}{\phi(t)}$, where $\phi(t)$ represents a function which depends only upon the temperature, and is independent of the nature of the substance used. The substance need not even be homogeneous throughout, but it may be heterogeneous, as, for instance, a mass of water and steam, or ice and water, or ice and steam; in these cases, however,

states, gaseous, liquid, and solid, it will be found that whenever any two of these states are present in contact together the pressure and temperature are dependent on each other, so that when one is given the other is fixed. Thus in Fig. 34 (Art. 141) we have a curve exhibiting in its upper part the relation between the temperature and pressure when water and steam exist together, and in its lower part the relation between the temperature and pressure when ice and steam exist together.

In addition to these we may have a third curve exhibiting the same relation when water and ice exist together, inasmuch as we know that the melting-point of ice depends upon the pressure. It would appear to result from this that these three curves must cross one another in one point and only one. To make this reasoning clear let us consider an ordinary case of ice and water at 0°C at the usual atmospheric pressure. May it not be said that here we have the three states of water substance together—namely, aqueous vapour, water, and ice? Unquestionably we have these three states side by side, but it is manifest that the atmospheric pressure does not represent the pressure of saturated vapour at the temperature of the experiment. But if we now reduce the pressure to that of saturated aqueous vapour at 0°C we raise by the same means the melting-point of the ice, so that the water in the experiment will gradually become ice. This prepares us to acknowledge that there is one point, and only one, where the three curves above mentioned can exist together, and therefore cut one another, and this is called by Professor James Thomson the triple point.

448. In Fig. 86 the ice-steam line is denoted by *NTQ*, the water-steam line by *PTL*, and the ice-water line by *MTR*, *T* being the triple point at which these three lines meet.

The first two of these lines have generally been regarded as one, and Regnault, we have already remarked (Art 145), was of opinion that his curve showed no peculiarity about this point. Nevertheless Professor Kirchhoff in 1858 and Professor James Thomson in 1871 were led, on different grounds and quite independently of each other, to believe that the ice-steam and water-steam lines are, in reality,

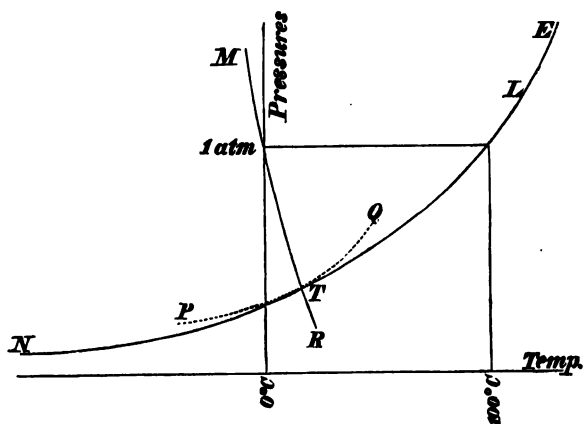


Fig. 86.

two distinct curves, crossing each other with a re-entrant angle at T .

The argument employed by the latter rests on the formula of Art. 341, viz. $\frac{\partial p}{\partial t} = \frac{M}{\phi(t)}$, where $\phi(t)$ represents a function which depends only upon the temperature, and is independent of the nature of the substance used. The substance need not even be homogeneous throughout, but it may be heterogeneous, as, for instance, a mass of water and steam, or ice and water, or ice and steam; in these cases, however,

466 *Tables of Pressure of Aqueous Vapour.*

Tempe- rature.	Pressure.	Tempe- rature.	Pressure.	Tempe- rature.	Pressure.
°	mm.	°	mm.	°	mm.
202	12733.69	212	15901.22	222	18053.64
203	12737.00	213	15977.48	223	18099.94
204	12740.30	214	16053.17	224	18146.07
205	12743.66	215	16128.33	225	18097.04
206	12747.12	216	16203.94	226	18142.92
207	12750.75	217	16279.15	227	18188.76
208	12754.53	218	16353.90	228	18234.61
209	12758.53	219	16428.29	229	18280.48
210	12762.50	220	16502.56	230	18326.40
211	12766.33	221	16576.13		

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TABLE III.

Shewing the pressure of aqueous vapour in millimètres of mercury at the latitude of Paris (48° 50') for each degree centigrade from -32°C to +23°C.

Tempe- rature.	Pressure.	Tempe- rature.	Pressure.	Tempe- rature.	Pressure.
°	mm.	°	mm.	°	mm.
-32	0.320	-1	4.263	30	31.548
31	0.352	0	4.600	31	33.406
30	0.386	+1	4.940	32	35.359
29	0.424	2	5.302	33	37.411
28	0.464	3	5.687	34	39.565
27	0.508	4	6.097	35	41.827
26	0.555	5	6.534	36	44.201
25	0.605	6	6.998	37	46.691
24	0.660	7	7.492	38	49.302
23	0.719	8	8.017	39	52.039
22	0.783	9	8.574	40	54.906
21	0.853	10	9.165	41	57.910
20	0.927	11	9.792	42	61.055
19	1.008	12	10.457	43	64.346
18	1.095	13	11.162	44	67.790
17	1.189	14	11.908	45	71.391
16	1.290	15	12.699	46	75.158
15	1.400	16	13.536	47	79.093
14	1.518	17	14.421	48	83.204
13	1.646	18	15.357	49	87.499
12	1.783	19	16.346	50	91.982
11	1.933	20	17.391	51	96.661
10	2.093	21	18.495	52	101.543
9	2.267	22	19.659	53	106.636
8	2.455	23	20.888	54	111.945
7	2.658	24	22.184	55	117.478
6	2.876	25	23.550	56	123.244
5	3.113	26	24.988	57	129.251
4	3.368	27	26.505	58	135.505
3	3.644	28	28.101	59	142.015
2	3.941	29	29.782	60	148.791

Temperature.	Pressure.	Temperature.	Pressure.	Temperature.	Pressure.
°	mm.	°	mm.	°	mm.
61	155.839	108	1004.910	155	4088.56
62	163.170	109	1039.650	156	4196.59
63	170.791	110	1075.370	157	4306.88
64	178.714	111	1112.090	158	4419.45
65	186.945	112	1149.830	159	4534.36
66	195.496	113	1188.610	160	4651.62
67	204.376	114	1228.470	161	4771.28
68	213.596	115	1269.410	162	4893.36
69	223.165	116	1311.470	163	5017.91
70	233.093	117	1354.660	164	5144.97
71	243.393	118	1399.020	165	5274.54
72	254.073	119	1444.550	166	5406.69
73	265.147	120	1491.280	167	5541.43
74	276.624	121	1539.250	168	5678.82
75	288.517	122	1588.470	169	5818.90
76	300.838	123	1638.960	170	5961.66
77	313.600	124	1690.76	171	6107.19
78	326.811	125	1743.88	172	6255.48
79	340.488	126	1798.35	173	6406.60
80	354.643	127	1854.20	174	6560.55
81	369.287	128	1911.47	175	6717.43
82	384.435	129	1970.15	176	6877.22
83	400.101	130	2030.28	177	7039.97
84	416.298	131	2091.94	178	7205.72
85	433.041	132	2155.03	179	7374.52
86	450.344	133	2219.69	180	7546.39
87	468.221	134	2285.92	181	7721.37
88	486.687	135	2353.73	182	7899.52
89	505.759	136	2423.16	183	8080.84
90	525.450	137	2494.23	184	8265.40
91	545.778	138	2567.00	185	8453.23
92	566.757	139	2641.44	186	8644.35
93	588.406	140	2717.63	187	8838.82
94	610.740	141	2795.57	188	9036.68
95	633.778	142	2875.30	189	9237.95
96	657.535	143	2956.86	190	9442.70
97	682.029	144	3040.26	191	9650.93
98	707.280	145	3125.55	192	9862.71
99	733.305	146	3212.74	193	10078.04
100	760.000	147	3301.87	194	10297.01
101	787.590	148	3392.98	195	10519.63
102	816.010	149	3486.09	196	10745.95
103	845.280	150	3581.23	197	10975.00
104	875.410	151	3678.43	198	11209.82
105	906.410	152	3777.74	199	11447.46
106	938.310	153	3879.18	200	11688.96
107	971.140	154	3982.77	201	11934.37

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